THE CHEMISTRY OF COLLOIDS

PART I
KOLLOIDCHEMIE

BY

RICHARD ZSIGMONDY

Professor at the University of Göttingen, Director of the Institute of Inorganic Chemistry

TRANSLATED BY

ELLWOOD B. SPEAR

Associate Professor of Inorganic Chemistry, Massachusetts Institute of Technology

PART II
INDUSTRIAL COLLOIDAL CHEMISTRY

BY

ELLWOOD B. SPEAR, B. A., PH. D.

A CHAPTER ON

COLLOIDAL CHEMISTRY AND SANITATION

BY

JOHN FOOTE NORTON, S. B., PH. D.

Assistant Professor of Chemistry of Sanitation, Massachusetts Institute of Technology

FIRST EDITION

NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

1917

Stanhope Press
F. H. GILSON COMPANY
BOSTON, U.S.A.

TRANSLATOR'S PREFACE TO PART I

In Part I it has been the endeavor to give an accurate translation of the German edition. The translation was submitted to, and approved by the author.

The translator wishes to acknowledge herewith valuable and painstaking assistance on the part of Edith Taylor Spear.

ELLWOOD B. SPEAR.

Cambridge, Mass.,
March, 1917.

TABLE OF CONTENTS

PART I

PART II

PART I

CHEMISTRY OF COLLOIDS

CHAPTER I

GENERAL CONSIDERATIONS

Definition of Colloids

In an article published in Philosophical Transactions in 1861, Graham * differentiated between crystalloidal and colloidal substances. To the first of these two classes belong those substances which exhibit an appreciable rate of diffusion and possess the property of penetrating membranes made of parchment paper. According to Graham the second group, colloids, comprises those substances which have no marked tendency toward diffusion, nor toward the penetration of membranes or gels.

Because of a large number of facts that have been discovered from time to time this classification can no longer be retained. On the one hand there are a great number of transitions between colloids and crystalloids, so that a sharp line can scarcely be drawn between the two domains. This difficulty, however, exists in many classifications other than that of Graham's. On the other hand there are many substances that will form colloidal or crystalloidal solutions depending upon the solvent employed. A classical example of this is sodium stearate, which has been studied by Krafft † and found to be a true crystalloid in alcohol, while it exhibits colloidal properties in aqueous solution. Other alkali salts of the higher fatty acids behave similarly.

From these and numerous other examples it follows that Graham's classification relates to mixtures rather than to chemically pure substances. A discussion of colloids from this point of view would have to do not with pure substances and their properties, but rather with those mixtures of substances which have colloidal properties. Ordinary chemical terminology also justifies this standpoint in that by colloidal silicic acid, gold, or platinum, for example, we understand not

* Th. Graham: Philos. Transact., 183 (1861); Liebigs Annalen, **121**, 1–77 (1862).

† See Chapter X.

the pure substances, but rather mixtures of silicic acid, gold, or platinum with water or some other medium; in other words, we mean colloidal solutions of these substances, or mixtures of them with protective colloids. Similarly gels, which are never chemical individuals, but are always mixtures of at least two substances, are classed as colloids. It is in general more exact to speak of colloidal systems than of colloidal substances, and to understand by the term " colloid " a colloidal system.

Nevertheless many pure substances may be regarded as crystalloids or colloids according to Graham's classification, if we but take into consideration that some of them when brought into contact with a given solvent always form a crystalloidal solution, while others invariably show colloidal properties in solution.

Behavior of Substances Toward Solvents

If the behavior of dry substances toward solvents is considered the following cases may be distinguished:

1. Many are either insoluble in the given solvent, or they dissolve spontaneously and form without exception crystalloidal solutions, *e.g.*, sugar or sodium chloride in water, benzoic acid in alcohol, naphthalene in benzol, gold in mercury.

2. Others when brought into contact with a given solvent remain undissolved, or they form spontaneously colloidal solutions only, *e.g.*, hemoglobin, albumin, dextrin in water; caoutchouc in benzol or carbon disulfide; resinates in ethereal oils. Substances of this sort even in a pure state can, without question, be considered as colloids according to Graham's classification.

3. There are, however, as already pointed out, some substances that occupy a position intermediate between classes one and two, in that they form crystalloidal solutions with some solvents and colloidal with others. In most cases of this sort the formation of a colloidal solution is caused by a chemical reaction between the substance in question and the solvent, whereby a compound is formed that is practically insoluble in the surrounding medium.

Irreversible Colloids. — It is of great importance to note that substances falling into class 1 can also be obtained in colloidal solution provided that such media are chosen in which the substance does not spontaneously dissolve; that is in which it is practically insoluble. This end can be arrived at by the employment of electrical energy, *e.g.*, Bredig's and Svedberg's methods for the preparation of colloidal metals. Or the same end may be achieved by means of chemical reactions whereby the substance is formed in a liquid in which it is

insoluble, *e.g.*, the preparation of colloidal gold, silicic acid, arsenious sulfide, silver iodide, etc. Naturally in the preparation of colloidal solutions of this sort certain well-defined procedures must be closely followed in order to obtain the substance in a finely divided state, and to prevent its immediate precipitation. Attention should be called here to the fact that colloidal solutions of this latter variety if they are pure, that is uncontaminated by the presence of any belonging to class 2, behave on being dried in a fundamentally different manner from those belonging to class 2. For, while the colloids of class 2 on drying leave a residue that will in general form the original colloidal solution, if brought in contact with the solvent, those in class 3 go through a series of irreversible changes of state during the drying process. As a result the residue has lost the property of again spontaneously forming the original colloidal solution with the liquid from which the residue was obtained. Colloids of class 2 are known as reversible, those of class 3 as irreversible, colloids.*

Colloids and Their Significance

In order to estimate the significance of colloidal chemistry it is necessary to introduce a number of substances, or systems of substances, that belong to colloids. In nature they are very widely distributed. All living matter, animal as well as vegetable, is for the most part built up of colloids. Without colloids life is impossible. Cells, their contents and membranes, consist of colloids. Blood serum and the sap of plants are intrinsically colloidal solutions. Glue, which is obtained from leather and bones, is a typical colloid. Hemoglobin, the red coloring matter in blood; rubber and guttapercha that flow from trees; vulcanized caoutchouc; starch and its by-product, dextrin; cellulose and its nitric acid ester, the explosive nitrocellulose; collodion, silk, wool, artificial silk, etc., are all colloids. Most of these are not simple substances but are none the less important for natural processes or for the industries. Furthermore the principal articles of man's food consist of colloids; proteids are colloids par excellence.

In the domain of inorganic chemistry also colloids are frequently met with, and although they are not so important as in the field of organic chemistry, especially that of organisms, nevertheless the study of these colloids greatly advanced our knowledge of the subject, chiefly because they lend themselves much better to investigation on account of the simplified conditions under which they can be obtained.

* W. B. Hardy: Zeit. f. phys. Chemie, **33**, 326, 385 (1900); Biltz: Ber., **37**, 1096 (1904); Zsigmondy: Zur Erkenntnis der Kolloide, 20 (1905).

Note. "Zur Erkenntnis der Kolloide" has been translated by Jerome Alexander under the title "Colloids and the Ultramicroscope."

In farming and various industries colloids play a very important part. According to van Bemmelen * it is the colloids in the soil that retain the food of plants and subsequently give it up to them. Fertilization with potassium carbonate and soluble phosphates, with saltpeter and ammonium salts would scarcely have any point for agriculture unless these salts were adsorbed by the colloids in the soil, and continuously imparted to the roots of the plants. Colloids have a very important bearing on the industries. As already indicated, a large number of the raw materials as well as the finished products belong to the field of colloidal chemistry. Many of the reactions involved in ceramics, glass making, dyeing, and certain other industries can be thoroughly understood only with a fundamental knowledge of colloidal chemistry. Moreover the study of colloidal chemistry has thrown considerable light on the cement and lime industries. The behavior of waste liquors from factories as far as the colloidal contents are concerned has become intelligible through investigations along the lines of colloidal chemistry. These investigations have resulted in new methods for dealing with the problems that arise in this field. Lüppo-Cramer † has pointed out that colloidal chemistry is responsible for an important awakening in photography. In physiology, in chemistry, in pharmacy, and in immuno-chemistry ‡ colloids have a prominent place. Indeed in almost every domain the new views with regard to colloidal chemistry are becoming general.

Graham's Characterization of Colloids

Because of the very wide distribution of colloids it is natural for investigators in almost all branches of science to turn their attention in the direction of the study of these substances. Botanists, zoölogists, physicians, and physiologists side by side with physicists and chemists have engaged in this work, and through the efforts of these considerable progress has been made. It is but necessary to call to mind the names Nägeli, Bütschli, van Bemmelen, Quincke, Hardy, Henri to show how many-sided are the problems presented in the field of colloidal chemistry.

To a chemist, Thomas Graham,§ belongs the credit of being the first to recognize and describe in detail the properties common to colloids. Although the two classes of solutions, colloidal and crystal-

* J. M. van Bemmelen: Landw. Vers.-Stat., **35**, 69–136 (1888).

† Lüppo-Cramer: Kolloidchemie und Photographie. Dresden (1908).

‡ H. Bechhold: Die Kolloide in Biologie und Medizin. Dresden (1912).

§ See page 3.

loidal, are closely associated by transitions, as pointed out on page 3, Graham's classification was the first to give a comprehensive survey of the differences between them. Here, as in many other cases, progress was coincident with, and dependent upon, the discovery of new methods. During his experiments Graham noticed striking differences in the rate of diffusion of various substances. He found that alkalis, acids, and salts, as well as sugar and alcohol, all crystalloids, diffused very rapidly compared with the slow rate of other closely allied substances which he called "fixed." The former he compared to volatile, the latter to less volatile, substances. Substances, such as dextrin, rubber, caramel, proteids, glue, etc., exhibited the further peculiarity of not (or at least with extreme slowness) diffusing through gels, plant or animal membranes. Because glue shows these and other properties common to colloids in an especially noticeable manner, Graham called this class of substances "colloids" after glue (Greek, kolla — glue, and eidos — appearance). Crystalloids, such as sugar, table salt, etc., on the other hand, pass through gels or membranes with extraordinary ease.

Graham based his method of separating colloids from the accompanying crystalloidal substances upon the differences in the rate of diffusion. This method he called dialysis. His apparatus, the dialyzer, is very simple. Moistened parchment membrane is brought over the edge of a cylindrical hard rubber ring, and bound with a string, thus forming a dish as shown in Fig. 1. The whole floats in a dish containing distilled water. The solution to be dialyzed is placed in the dish made of the membrane and the rubber ring, and allowed to float on the surface of the distilled water for some time. If one subjects to dialysis a mixture of sugar and gum arabic, both dissolved in water, the sugar diffuses gradually into the outer vessel and the gum arabic remains behind. It is now only necessary to change the water frequently and to allow the dialysis to continue until no more crystalloids (in this case sugar) pass from the inner to outer vessel. If one begins with a suitable mixture, *e.g.*, a solution of sodium silicate saturated with hydrochloric acid, it is possible to obtain the colloid in a fairly pure state, the colloid being, in this case, silicic acid. Small amounts of electrolytes almost always remain behind; the significance of which we shall deal with later on.

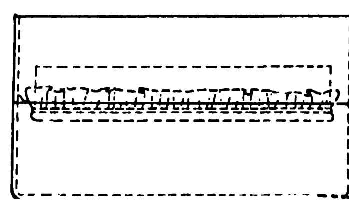


FIG. 1. Graham's Dialyzer.

Definitions

Colloidal solutions obtained in this manner with water as a solvent Graham called "hydrosols." If alcohol is used instead of water alcosols are obtained. In general colloidal solutions where organic solvents are employed are called organosols. Colloidal solutions are frequently designated by the term sol. A noteworthy property of many colloidal solutions is the tendency to form a jelly-like half solid mass, when a large portion of the solvent is removed, or when the solution is subjected to the influence of salts or other foreign bodies. From hydrosols hydrogels, from alcosols alcogels, are obtained. On further drying the apparently amorphous solid residue may be transparent and glassy, crumbling and porous, or in the form of a powder. These largely dehydrated residues are usually referred to as hydrogels, or, more generally, gels, even if they no longer have the property of becoming spontaneously dispersed in the original solvent. The dried residues of reversible colloids are called solid sols by Lottermoser.*

Coagulation. — Coagulation, the change of concentrated irreversible hydrosols to a jelly-like state, often occurs spontaneously. This process closely resembles the crystallization of a very soluble salt from a supersaturated solution by inoculation with a tiny crystal. Frequently the process takes place slowly, allowing the coagulation to be followed step by step. Coagulation may occur in dilute solution also and in these cases amorphous precipitates are obtained instead of jellies. At the temperature of the coagulation these amorphous precipitates are not soluble in an excess of the solvent, or at least to a very limited extent. Coagulation is therefore an irreversible change of state of colloids.

Peptisation. — Under the influence of sometimes very small quantities of foreign substances hydrogels may be changed into hydrosols. Having in mind the formation of peptones from proteids by means of HCl, Graham called this reaction peptisation.† Many differences between the dissolving of colloids and crystalloids are easily discernible. If a crystal is dipped into a solvent in which it will dissolve, for instance NaCl in water, it will be seen that the crystal, without taking up any of the solvent, gives its outside layers to the surrounding liquid. At any moment the residual piece has the exact composition of the original crystal. The analogy to the evaporation of a volatile substance is far reaching and has long been recognized. Re-

* A. Lottermoser: Über anorganische Kolloide, 2. Stuttgart (1901).

† Graham: Proc. Roy. Soc., 16, June (1864); Poggendorffs Annalen, 123, 529–541 (1864).

versible colloids, on the other hand, behave in quite another manner toward solvents. Particles of the solid are given up to the liquid, it is true, but the solid also takes up considerable amounts of the liquid. Colloids distend before they dissolve and this swelling process has in many cases been closely studied. The gels of many reversible colloids formed by swelling, gelatin for instance, dissolve only on raising the temperature; others go into solution at room temperature, *e.g.*, gum arabic.

The reverse processes on evaporation follow similar lines. From a sufficiently concentrated solution of NaCl crystals separate out directly and have the same composition as the original substance dissolved to form the solution. On the other hand solutions of glue, rubber, etc., during evaporation pass through several intermediate steps between the liquid and solid states, before they finally become congealed. In a solid state colloids always retain a portion of the solid or medium, but never in stoichiometric relations such as exist between crystals and their water of crystallization. We see, therefore, that crystalloids pass directly from the solid to the liquid, and back again from the liquid to the solid state, while colloids go through a gradual change, involving innumerable intermediate steps. At this point a misconception for which Graham's terms, crystalloid and colloid, are responsible, should be called to the attention of the reader. Graham rightly remarked that colloidal solutions generally leave behind an amorphous (better amorphous appearing) mass, or residue. From this it is sometimes concluded that colloids never crystallize. This is not correct, for when certain precautions are taken crystals may be caused to grow in many colloidal solutions. Crystallized albumin, globulin, hemoglobin, etc., exist, and even from solutions of colloidal silver crystals of silver may be obtained. Furthermore the amorphous appearing residues may be in no way truly amorphous, but rather consist of ultramicroscopic crystals that appear to be amorphous merely because the microscope reveals aggregations of crystals and not the individuals.

Differences Between Solutions of Irreversible Colloids and those of Crystalloids

The preparation of irreversible hydrosols indicates that they differ in many respects from solutions of crystalloids. For, while the latter are obtained directly by dissolving the solute in the solvent, roundabout methods are necessary in the former case to procure a state of fine subdivision. In point of fact closer investigations have shown that irreversible hydrosols do not in general exist in a state of molec-

ular dispersion as is the case with crystalloids, but that in the solution all possible sizes of particles occur from the molecular to those of microscopical dimensions. These differences were noticed at an early stage and the endeavor was made to characterize both reversible and irreversible hydrosols as suspensions, in contradistinction to the unquestionably homogeneous crystalloidal solutions. In the opinion of the author this term is not suitable to characterize accurately nor correctly the field with which we are concerned. It is based on a restricted point of view, and does not take into consideration the fact that the properties of matter undergo considerable change when the particles are further subdivided. Moreover it is not in accord with the common usage among chemists.

Reversible and Irreversible Colloids

The fact that both reversible colloids and crystalloids go into solution spontaneously would lead us to believe that they are closely related, and differ probably only in the matter of molecular weight. Graham expressed this idea, and many others have the same point of view. It is, however, only a part of the truth. In point of fact there are certain colloids where there are good grounds for assuming that the subdivision during solution reaches molecular dimensions, but the particles are so large that they cannot pass through parchment or collodion membranes. Hemoglobin of cattle is an example; the molecular weight was found by three methods to be in the neighborhood of 16,500.* The methods are given on page 233. Another instance similar to this is that of soluble starch.

In general large molecules have the tendency of uniting to form still larger aggregates. This tendency, which is so in evidence in the formation of gels, nature makes use of in the building up of animal tissues. Animal fluids, such as blood, milk, etc., contain in addition to the microscopical blood corpuscles, fat particles, etc., a myriad of much smaller bodies that can be distinguished by means of the ultramicroscope. Solutions of many reversible colloids, such as globulin, gelatin, and many solutions of natural and artificial coloring matters, are filled with submicroscopical particles that, in the main, are larger than those found in gold hydrosols. In characterization of reversible colloids it is necessary to add that irreversible colloids may become reversible by the addition of other reversible colloids.

From what has been said it cannot be concluded that solutions of reversible colloids more nearly approach the crystalloidal condition than do those of the irreversible, although certain dry residues of the

* See Chapter XII, page 233.

former have the property of forming the original sol with the solvent. Neither is it in accordance with the facts to imagine a greater similarity between suspensions and irreversible colloids than between suspensions and reversible; nor is it true that irreversible colloids contain larger particles than the reversible. On the contrary it is theoretically possible to prepare irreversible hydrosols with greater dispersion, or homogeneity, than exists in solutions of some of the reversible colloids, even when the subdivision of the latter reaches molecular dimensions as in the case of hemoglobin from the blood of cattle.

Preparation of Colloidal Solutions

Colloidal solutions may be made by many different methods. The least difficult of these is the preparation of the hydrosol of a reversible colloid. If the dry colloid in question is brought in contact with the medium, or solvent, the dissolution occurs spontaneously. In this way colloidal solutions of rubber, dextrin, proteids, molybdic acid, tungstic acid, Lea's colloidal silver, Paal's colloidal gold, and many others may be obtained. Hydrosols may be made from the hydrogels of irreversible colloids by peptisation, provided that the dehydration has not been carried too far; in which case the new colloidal solution may be obtained only by the employment of roundabout ways. In the case of metals colloidal solutions are often made by electrical colloidation (sparking, atomization), while others are obtained by chemical means. Thus, dehydrated silicic acid may be changed into a soluble silicate by fusing with alkali. The aqueous solution of this is treated with HCl, and subsequent dialysis yields the corresponding hydrosol. Hydrosols of metals can also be prepared by dissolving the metal in a suitable acid, and carefully reducing the compound according to well-defined procedures. Methods of this sort may be called, according to Svedberg,* condensation methods, while the electrical colloidation according to Bredig or Svedberg is a dispersion method. The preparation of specific colloids will be taken up more fully in the chapters comprising the special part of this work.

Optical Properties

Well-prepared colloidal solutions are transparent or slightly opalescent, and may be either colored or colorless. They readily pass through filter paper without leaving a residue. Every cubic millimeter of a definite colloidal solution has identical properties with, and gives precisely the same reactions as, every neighboring portion.

* The Svedberg: Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe. Dresden (1909).

Within macroscopical limits colloidal solutions are homogeneous, and appear so under the ordinary microscope. Nevertheless almost all colloidal solutions are found not to be homogeneous if investigated by means of the Tyndall effect. This inhomogeneity can vary markedly in different solutions of one and the same colloid without involving a corresponding change of properties or chemical reactivity. In fact it is possible to obtain with one and the same substance either hydrosols in which the optical inhomogeneity can scarcely be observed or those that possess a distinct turbidity.

The ultramicroscope affords an opportunity for the closer examination of the nature of the diffusion of light rays by hydrosols, and gives a glimpse into the spacial discontinuity in these systems. The mere presence of this discontinuity could be foretold by the Tyndall effect, but it remained for the ultramicroscope to reveal the fact that colloidal solutions contain small individual particles in rapid motion, the size of which particles is somewhat larger than the molecules in crystalloidal solutions. The investigation of hydrosols with this instrument has made possible much more definite ideas with regard to the size, color, polarization, motion, etc., of these particles, and permitted the scientist to enter a field that had been practically closed to him. However, some of the particles present in the hydrosols are so small that they cannot be detected even by the ultramicroscope, and this led to a further subdivision of particles according to whether or not they could be seen by this means.

Ultramicrons. — According to the nomenclature suggested by Siedentopf,* particles smaller than the resolving power of the ordinary microscope are called ultramicroscopic, regardless of whether they are visible under the ultramicroscope or not. These particles are called submicroscopical if they can be seen, and amicroscopical if they cannot be seen by the ultramicroscope. According to the suggestion of the author,† submicroscopical particles are known as submicrons, and amicroscopical as amicrons.

Colloidal solutions of metals lend themselves particularly well for ultramicroscopical examination because of the marked difference in the optical constants of the disperse phase and the disperse medium. It is possible to render the particles in ruby glass visible although they are only about 6 $\mu\mu$ in diameter. The limits of visibility are reached much sooner in the case of colloidal oxides, and as a general rule in the organic colloids also. Ultramicroscopical particles of such hydrosols become amicrons at a diameter of about 30–40 $\mu\mu$.

* H. Siedentopf: Berl. klin. Wochenscher, Nr. 32 (1904).

† R. Zsigmondy: Zur Erkenntnis der Kolloide, 87 (1905).

Ultramicroscopy

Ultramicroscopical particles of not too small diameter can be rendered visible by a simple method which has been described by the author in his publication, "Zur Erkenntnis der Kolloide." For very small submicrons a good ultramicroscope is essential. Fig. 2 is a diagram of the ultramicroscope according to Siedentopf and Zsigmondy.*

The source of light is an arc lamp, or, still better, the sun. The telescope objective F_1 throws an image of the source of light on the bilateral slit S. A second telescope objective F_2, having a focus of

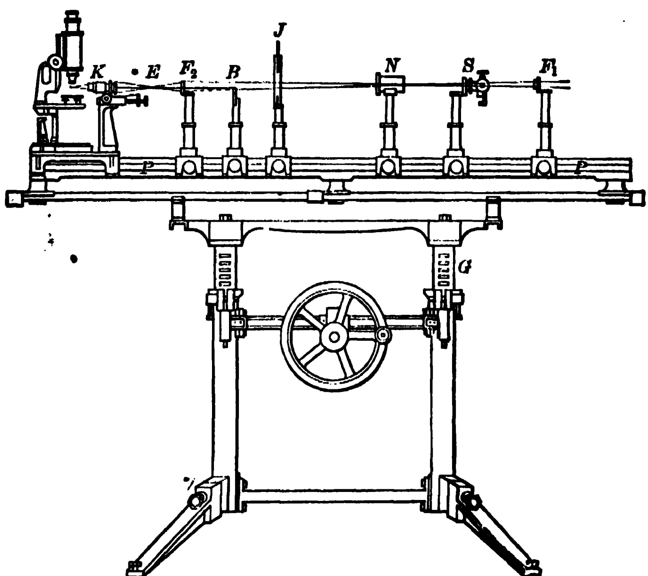


FIG. 2. Slit ultramicroscope.

about 80 mm., forms a real image of the slit in the plane E of the condenser K. A microscope objective serves as a condenser K, which throws a reduced image of the slit in the solution. The objective of the observation microscope is adjusted over this image. J and B are screens, while N is a Nicol's prism, which is not necessary for ordinary work. The preparation to be investigated is put into a tiny cuvette which can be raised or lowered at will, and is shown in Fig. 3. The cuvette is attached to the objective of the observation microscope in such a manner that they can be raised or lowered simultaneously by

* H. Siedentopf und R. Zsigmondy: Drudes Annalen d. Phys. (4), 10, 1–39 (1903).

means of the adjusting screws. This arrangement not only facilitates rapid and easy adjustment, but permits the examination of a number of liquids without any further adjustment of the apparatus. It is merely necessary to wash out the cuvette by allowing water or other cleaning liquid to run through it and to refill it with the solution in question. For full directions with regard to the necessary manipulation the author refers to his already cited publication, and to a pamphlet issued by the optical works of Carl Zeiss (Sign. M 229, Jena, 1907). One learns best of all from an experimenter who has had some experience with the instrument.

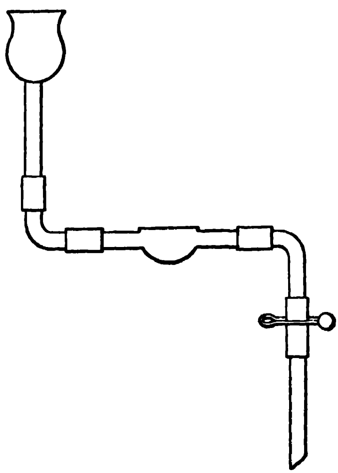


FIG. 3. Cuvette.

Among other ultramicroscopical arrangements that have been constructed is that of Cotton and Mouton. With a simple piece of apparatus they have carried out a series of important experiments concerning the electrical migration of colloids, and the magneto-optical properties of hydrosols, especially in the case of colloidal iron oxide. Cotton and Mouton published their investigation * in 1906, fully describing the apparatus employed. The incident rays are reflected from a glass prism and form an image of the source of light between the cover glass and the stage of the microscope. The rays do not enter the microscope because they are totally reflected by the surface of the cover glass.

Likewise between the cover glass and the stage of the microscope bacteria are made visible by means of an apparatus according to Siedentopf.† For similar purposes are employed the dark field illumination with a mirror condenser of Reichert,‡ Ignatowsky,§ the cardioid condenser of Siedentopf,¶ and the concentric condenser of Jentzsch.|| The three condensers last mentioned illuminate the preparation to an almost theoretical degree of intensity. All these instruments have the disadvantage, however, that dust particles, adsorbed

* A. Cotton et H. Mouton: Les ultramicroscopes et les objects ultramiscopiques. Paris (1906).

† H. Siedentopf: Zeit. f. wiss. Mikroskopie, **24**, 104–108 (1907).

‡ C. Reichert: Zeit. d. Allg. Österr. Apoth. Ver., Nr. 6 (1908).

§ W. v. Ignatowsky: Zeit. f. wiss. Mikroskopie, **26**, 387-390 (1909).

¶ H. Siedentopf: Verh. d. Deutsch. Phys. Ges., **12**, 6–47 (1910).

|| F. Jentzsch: Verh. d. Deutsch. Phys. Ges., **12**, 875–991 (1910).

ultramicrons, etc., interfere with the observations, and the preparation of the material sufficiently pure for investigation is, therefore, very difficult.

Polarization by Small Particles; Tyndall's Phenomenon

If an unpolarized ray of light falls on a colloidal solution a certain amount of diffusion of the ray takes place, and the reflected light ray suffers plane polarization. This phenomenon is true in general for all disperse systems as long as the diameter of the particles is small compared to the length of the light waves, and as long as the refractive index of the disperse phase differs from that of the disperse medium. Plane polarization of light by small particles has long been known as the Tyndall effect. We know from the experiments of Tyndall that the polarization becomes more pronounced with the diminishing size of the particles, and is complete only when their diameter is small compared with the length of the light waves. Tyndall studied the phenomenon with jets of steam where the size of the particles could be varied at will. Rayleigh expounded the theory of this polarization and found that the intensity of the reflected ray was inversely proportional to the fourth power of the wave length. He found further that the illumination from any one particle was proportional to the square of the volume of the particle. That is, the shorter waves were more refracted than the longer, and the illumination from the particles became rapidly less as the size decreased. It is a well-known theory that the blue of the sky is due to the refraction of light rays by small particles. According to Rayleigh these particles may be oxygen molecules. This refraction was at first held by many to be fluorescence. The Nicol's prism enables the distinction to be made very easily between the two phenomena.

The Determination of the Size of Ultramicroscopical Particles

Conditions essential for successful experimentation with colloidal solutions will be found comprehensively described in the already cited publication of the author, Chapter 6. The size of the particle is most easily determined by counting the number of them in a given volume of the hydrosol and applying the formula

$$L = \sqrt[3]{\frac{A}{S \cdot N}},$$

where L is the length of the side of one particle, A is the mass of the dispersed substance in the unit volume, N the number of submicrons in the same volume, and S is the specific gravity of the dispersed sub-

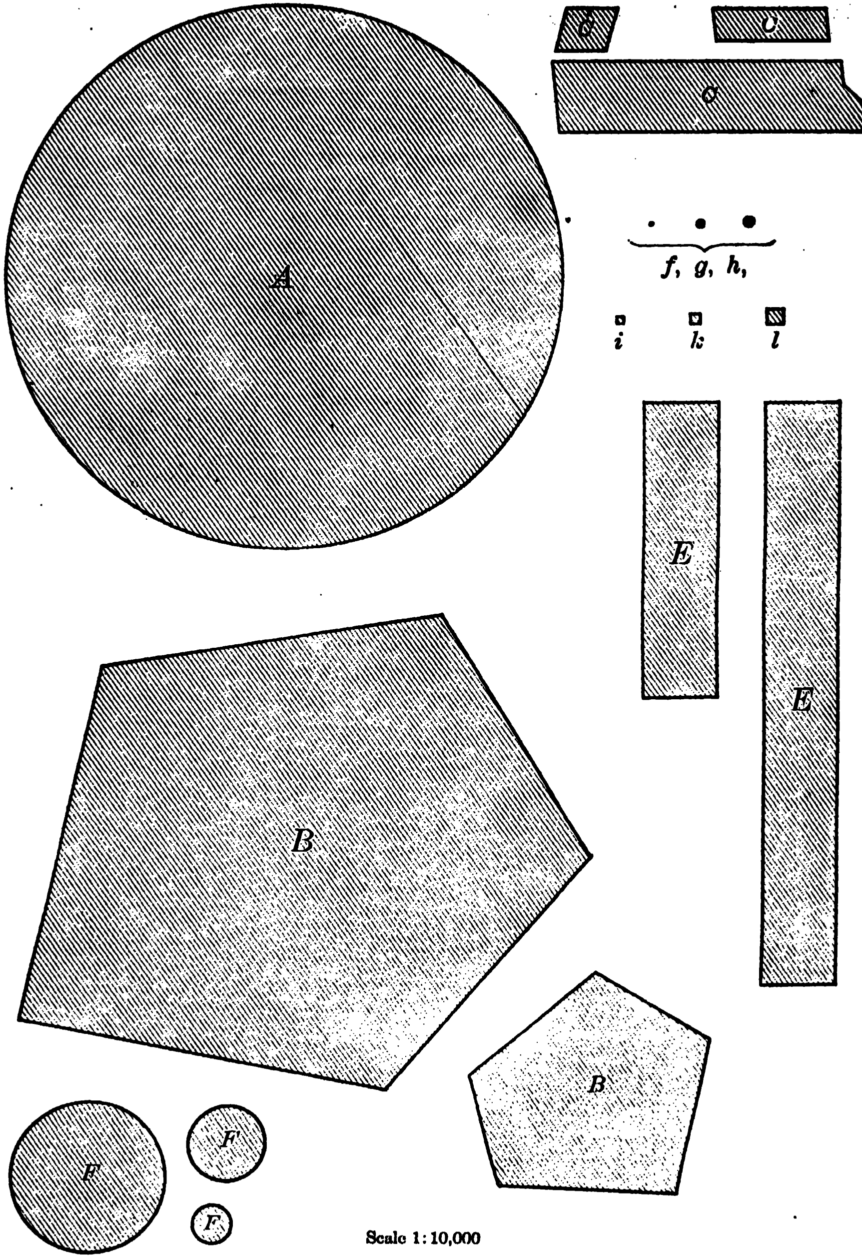
stance. The formula holds under the assumption that the particles are cubical in shape, and that they are uniformly distributed.* A further assumption is made that the particles are visible and exactly alike. If the particles are not all visible and the large majority are submicrons, the result obtained represents the upper limits. On the other hand, if the majority of the particles are not visible the result will be very wide of the mark. By closely following the directions it is possible to arrive at a useful result for the average size of the particles. Wiegner † has shown that by counting the particles of suitable gold hydrosols different experimenters at different times with the same solution obtain results agreeing with one another within the experimental error.

The extraordinary difference in size of the particles in ordinary suspensions and those in hydrosols may be realized from Table 1, which is taken from the author's‡ publication already cited. In Table 2 the linear dimensions of ultramicroscopical gold particles are compared to those of the molecules. The figures require no further explanation.

* H. Siedentopf and R. Zsigmondy: Drudes Annalen (4) **10,** 16–29 (1903).

† G. Wiegner: Kolloidechem. Beihefte, **11,** Heft, 6–7, 213–242 (1911).

‡ R. Zsigmondy: Zur Erkenntnis der Kolloide, 122. Jena (1905).

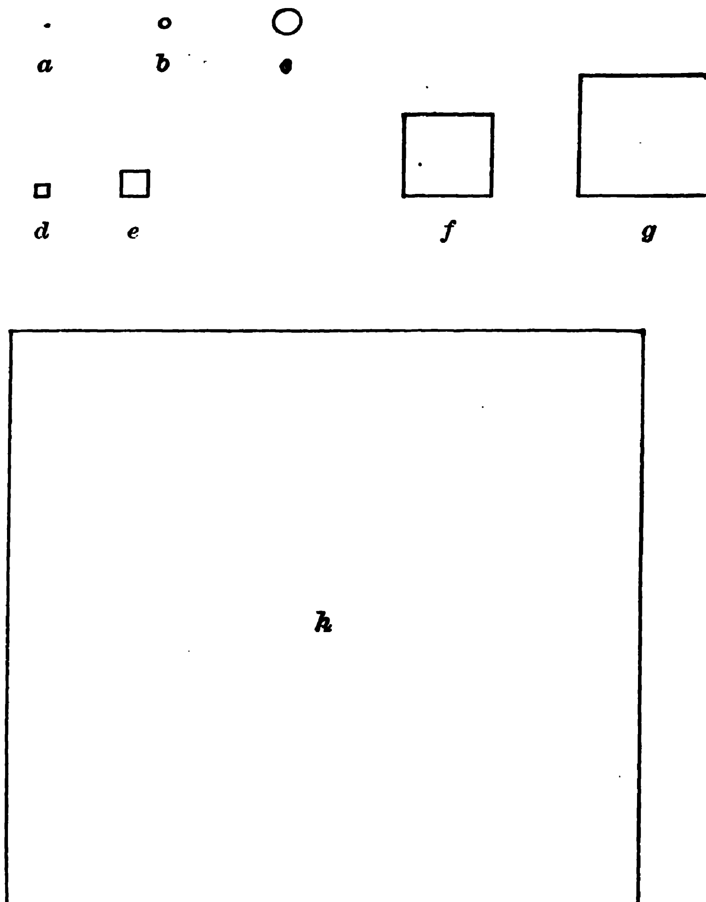


Scale 1:10,000

DIAGRAM 1.

A. Corpuscles in human blood.
B. Fragments of rice starch.
C. Particles in kaolin suspensions.
E. Bacilli from a diseased spleen.
F. Globular bacilli.
f, g, h. Particles in colloidal gold.
i, k, l. Particles that precipitate from gold suspensions.

2202



Scale 1 : 1,000,000

DIAGRAM 2.

a. Hydrogen molecules.
b. Chloroform molecules.
c. Hemoglobin molecules.
d, e, f, g. Particles in colloidal gold.
h. Particles that precipitate from gold suspensions.

CHAPTER II

CLASSIFICATION

Change of Properties of Dispersed Systems with the Size of the Particles

It is a well-known fact that the properties of rock fragments differ with the size of the fragments. Geologists group the fragments broken off from rocks into boulders, rubble, pebbles, gravel, sand, and dust, employing as a basis the change of properties with the size of the individual pieces. For instance, sand and dust are transported by the wind, while the others remain behind. The material of which these particles are composed makes little difference. Again sand will pass through a sieve of 10 mm. gauge, and the others will not. In the case of smaller subdivisions also with which we are interested striking changes of properties occur with changes in the size of the particles. Dust or kaolin stirred in water causes a turbidity and will gradually settle to the bottom. Hydrosols in which the particles are less than 20 $\mu\mu$ remain quite clear and do not settle at all. It is a well-known fact that between these very fine subdivisions, on the one hand, and coarse suspensions on the other, there exist all possible intermediate steps. All these subdivisions may be included in the large group of dispersed systems. Nevertheless the classification of colloidal systems demands further grouping because the typical representatives of these groups have very different properties.

A scientific basis for classification would be the division into groups where sudden changes of properties occur,* or where there is a marked change in any one property. Fortunately such sudden changes, or breaks, do occur. For instance if one chooses the diameter or size of the particles as a gradually changing property, a sharp break occurs between the limits 0.1 μ and 1.0 μ, as will be seen by the following considerations. The resolving limit of the best microscope is reached at 0.2 μ, and therefore the actual form of particles smaller than this cannot be seen. In this neighborhood also lies the limit of visibility with the microscope, using ordinary light. As a result of this coincidence these two limits have often been confused. The limit of visi-

* W. Ostwald: Koll.-Zeit., 1, 297 (1907).

bility by means of the microscope in transmitted light is, however, of great importance because the presence of tiny particles, such as occur in colloidal solutions, could not be proved until the introduction of ultramicroscopy. Previous to this microscopic observers considered such systems homogeneous. Even chemists accepted these limits, and systems in which the microscope no longer gave indications of the existence of individual particles were classified among the homogeneous.

At a very slightly lower limit than the above, particles with even a high specific gravity no longer sink to the bottom in water, but re*main suspended, and in constant vibration. At a slightly higher limit than this lies the value beyond which the Brownian movement is too* small to be perceived. Another limit of importance to the chemist is 1.0 μ, because particles larger than this may be separated from the medium by filter paper. If all this is taken into consideration it will be seen that particles appreciably smaller than the light waves have entirely different properties from those that are larger, and that a number of properties manifest a more or less sudden change in the region of the resolving limits of the microscope. A brief summary of these relations is given in Table 1.

TABLE 1

0.1 $\mu\mu$	1 $\mu\mu$	10 $\mu\mu$	100 $\mu\mu$	1 μ	10 μ	100 μ	1 mm.

Ultramicroscopic field	Microscopic field Real form of particles may be seen.
Quartz in solution does not form a sediment	Quartz solution forms a sediment
Oil emulsions in water do not separate into two layers	Oil emulsions in water separate into two layers.
Particles pass through filter paper	Particles may be filtered out

Brownian Movement

Very rapid		Slow		None
Crystalloidal solutions	Hydrosols Colloidal Solution	Turbidities		Suspensions

From a brief review of the systems, that up to the present time have been considered hydrosols, it will be seen that few have been ascribed

to this class where the individual particles could be seen under the ordinary microscope, because sedimentation takes place even when the subdivision is still very fine. Especially is this the case if the specific gravity of the disperse phase is appreciably greater than that of the disperse medium. It is therefore possible without reserve to set 0.1 μ as the upper limit of size for the particles in a true hydrosol.* The single exception is that of drops of oil in water. Without question the majority of Graham's colloidal solutions, if carefully prepared, have a much greater degree of homogeneity, and contain much smaller particles.

From a consideration of the fact that only homogeneous appearing *mixtures are classified by chemists and physicists as solutions, it* would be well to retain the term "colloidal solution" for systems having this apparent homogeneity, and, following the suggestion of Quincke,† to designate as turbidities all sols where a turbid appearance indicates inhomogeneity; that is all systems that occupy a position intermediate between colloidal solution and true suspensions. We have, therefore, the following approximate limits:

True suspensions with particles down to about 0.1 μ.
Hydrosols (colloidal solutions and turbidities) with particles between 0.001 μ and 0.1 μ.
Molecules of crystalloids with particles between 0.1 $\mu\mu$ and 1.0 $\mu\mu$.

It is obvious that the division into groups gives only an approximate survey of the size relations appearing in different sorts of finely divided systems, and that a sharper subdivision of dispersed systems based on the size of the particles would be fraught with difficulties, because the properties of finely divided matter are not completely determined by the size of the particles. A number of other factors must be included that depend upon the nature of the dispersed material, the disperse medium, and the presence of other substances. From a consideration of these circumstances, without ascribing any particular size to the particles, one may assume that a given system belongs to the colloidal, if the effect of gravity is negligible compared to the influence of kinetic and other forms of energy; that is, when the last-named factors determine the behavior of the system.

Suspensions and Hydrosols

The influence of the size of the particles is especially marked when subdivisions are compared, the particles of which belong to a differ-

* G. Wiegner: Zeit. f. Kolloidchemie, Beihefte, **2,** 213–242 (1911).
† G. Quincke: Drudes Annalen d. Phys. (4), **7,** 57–96 (1902).

ent order of magnitude; that is, when colloids are compared with suspensions that settle out rapidly. Because a great deal of misapprehension exists with regard to the behavior of true coarse suspensions, the subject will be taken up briefly at this point.*

Coarse Suspensions. — Frequently the behavior of irreversible colloids is considered analogous to that of coarse suspensions, although the latter may manifest little or none of the properties of the former. *The study of the properties of such suspensions, which may be carried on to advantage with potato starch (freed from smaller particles),* where the particles have a diameter lying between *0.03 and 0.1 mm.*, or with quartz suspensions with particles between 0.1 and 0.2 mm., reveals little save sedimentation. Electrolytes either cause no perceptible change in the coagulation, or they retard it because of the increased density of the medium. Such suspensions are as insensitive to electrolytes of medium concentration as are proteid solutions.

In the case of finer suspensions such as wheat starch or quartz powder, the particles of which have a diameter of 0.001 to 0.005 mm., the effect of electrolytes is more marked. The particles flock together to form larger aggregates, and these aggregates precipitate more rapidly than do the individual particles. The much investigated turbid solutions of clay exhibit this to a marked degree, as shown by the work of Schlösing † and Bodländer.‡ These solutions behave in a manner very similar to that of irreversible hydrosols such as colloidal metals, which are also very sensitive to the action of electrolytes.

The statement so often met with in the literature that the precipitation of these finer suspensions is irreversible, as in the case of colloidal metals, is quite false.§ Schlösing has demonstrated that after the removal of the electrolyte the clay may be returned to its original suspended form. In this regard turbid clay solutions resemble hydrophile colloids (reversible) much more than they do metal hydrosols, and from the properties of the precipitate should be classed with the former rather than with the latter. The similarity between turbid solutions of clay and metal hydrosols exists almost exclusively in the sensitivity of both toward electrolytes. This sensitivity, however, they have in common with certain ionogen disperse solutions such as Congo-red and Benzopurpurin.

* Zsigmondy: Zur Erkenntis der Kolloide, 11–16.

† Ch. Schlösing: Compt. rend., **70**, 1345–1348 (1870).

‡ G. Bodlander: Neues Jahrb. f. Min., Geol. usw., **2**, 147–168 (1893); Nachrichten d. Kgl. Ges. d. Wiss. Göttingen. Math. phys. Kl., 267–276 (1893).

§ Z. B. Wo. Oswald: Grundriss der Kolloidchemie, 101–102. Dresden (1909).

Similarities between Colloidal and Crystalloidal Solutions

Although the want of homogeneity, together with some other properties has been the occasion for considering colloidal solutions as discontinuous, one is not justified in choosing this property as a characteristic distinction between colloidal and crystalloidal solutions. For, on the one hand, the optical inhomogeneity of hydrosols can be made almost to disappear; while, on the other, as Spring, Lobry de *Bruyn, and their fellow workers have shown, a large number of crystalloidal solutions exhibit the Tyndall effect quite as well as colloidal* solutions do.

The existence of all manner of gradations between the two extremes, colloidal and crystalloidal solutions, is still further ground which goes to show that a fundamental distinction between these two classes of solutions is impractical. Finally, from a geometrical point of view such a distinction would be possible only on the assumption that crystalloidal solutions are continuous. This hypothesis is not tenable because there can no longer be any doubt as to the existence of molecules.*

From what has been said it is evident that the question, whether hydrosols are solutions or suspensions, is purposeless. As a matter of fact they occupy an intermediate position. They exhibit properties that resemble crystalloidal solutions or suspensions depending upon the kind of hydrosol and upon the fineness of division. As Nernst † has often pointed out, the general behavior of most colloidal solutions would place them with the crystalloidal rather than with suspensions. The fact that hydrosols diffuse, and that they possess osmotic pressure would tend to justify this point of view.

Electrical charges on the particles operate in such a manner that many hydrosols behave during electrolysis precisely as electrolytes with large complex ions. Colloidal stannic acid, the purple of Cassius and many others may be cited as examples. The reactions of hydrosols are often determined by the electrical charge and are generally characteristic of the sign. They are dependent upon the nature of the disperse phase just as in the case of crystalloidal solutions. The particles of reversible and also the irreversible hydrosols behave similarly to molecules and ions in that they are adsorbed by various substances.

Although the occurrence of sudden breaks in the properties of the solution marks the noticeable difference between a typical colloidal and crystalloidal solution, nevertheless these same sudden breaks are

* W. Mechlenburg: Die experimentelle Grundlegung der Atomistik. Jena (1910).

† W. Nernst: Theoretische Chemie, 5. Aufl., 415.

also met with in systems having properties intermediate between the two main classes. For instance breaks occur in the case of suspensions in the neighborhood of the resolving power of the microscope, while this same phenomenon is manifested in crystalloidal solutions where the particles have the dimensions of about 1 $\mu\mu$.

Behavior of Hydrosols on Evaporation

As has already been pointed out on page 10, colloids can be divided *into the two classes*, reversible and irreversible, depending upon *whether or not they leave a soluble residue on evaporation. The irreversible can be still further divided into two groups. 1. To the* first class belong those that coagulate in dilute solution, and precipitate in the form of a powder rather than a jelly. Examples of these are the colloidal metals in a pure state (colloidal metals that are not rendered impure by the presence of any other colloid). 2. The second class consists of those that may be considerably concentrated before coagulation sets in and whose precipitates are decidedly jelly-like, such as colloidal silicic acid, stannic acid, clay, iron oxide or hydroxide.

Colloids of the first group, which may be considered as completely irreversible, are coagulated by all of the well-known methods, such as evaporation, addition of an electrolyte, freezing, etc. The coagulation is so thorough that the colloid cannot be brought back into its original state either by raising the temperature, by dilution with water, removal of the electrolyte, or by peptisation. In order to make a hydrosol out of the residue electrical or chemical energy is imperative.

With the irreversible colloids of the second class, on the other hand, it is possible to reform the hydrosol by the addition of a small amount of a suitable reagent provided that the residue has not been too thoroughly dehydrated. A too complete dehydration causes a continuous change to take place which may proceed so far that the dry residue will no longer undergo peptisation. (Example, colloidal stannic acid.)

Lying in a position intermediate between hydrosols of pure metals and irreversible oxides will be found the majority of well-dialyzed sulfide hydrosols. On evaporation these sometimes give jelly-like bodies and sometimes precipitate in a powder form.

Typical reversible colloids, after sufficient swelling has occurred, dissolve in a solvent to give a homogeneous appearing hydrosol. Gum arabic, albumin, hemoglobin, and Paal's colloidal palladium are good examples. Substances, such as glue, soluble starch, gelatin, agar-agar, and many others, constitute a special class of reversible colloids

that have the peculiarity of hardening into the form of a gel on cooling. The dried residue of these bodies will swell up to a certain degree in water at ordinary temperatures, but the raising of the temperature causes complete and easy dissolution. In fact the frequent occurrences of bodies having this peculiarity led Graham to choose glue as the typical representative of colloids.

Another class of reversible colloids deserves mention. They may be called half- or semi-colloids because they diffuse in water very slowly through membranes. They also exhibit a certain amount of *osmotic pressure, and lower the boiling point appreciably. These properties would place them in a position midway between colloids* and crystalloids. A large number of substances belong to this class; on the one hand decomposition products of true colloids, such as dextrin and peptones; on the other, aqueous solutions of salts of organic substances possessing high molecular weights, such as stearic and oleic acids, and the salts of acid and basic dyestuffs. Salts of dyestuffs are perhaps to be regarded as mixtures of colloids and crystalloids. Soap in water doubtless belongs to this class.*

The Behavior of the Specific Groups Toward Electrolytes

No very general statement can be made with regard to the effect of electrolytes on hydrosols. It is possible, however, to enunciate a large number of laws, which have many exceptions when specific groups are considered.

A. Irreversible Colloids. — Some irreversible colloids are sensitive to electrolytes, while others remain unaffected. Some degree of regularity of behavior is manifested only by colloidal metals (free from contamination with other colloids), salts, and sulfides. Here the law obtains with a fair amount of certainty, that electrolytes cause precipitation. In general very small concentrations of salts, bases, and acids suffice to coagulate the colloid in question. The precipitate is not soluble in water. Nonelectrolytes, on the contrary, usually do not cause coagulation. The sensitiveness may be completely destroyed by the addition of often very small quantities of protective colloids. Even traces of these last-named substances may influence the reaction to a considerable degree.

Colloidal oxides in part obey the above law; in part show a specific behavior for each individual case. For instance colloidal stannic and ferric oxides are immediately precipitated by most electrolytes; while silicic acid, zirconium and thorium oxides, and many others show

* McBain: Jour. Chem. Soc., 101, 2042 (1912).

specific reactions. Whether the product of the precipitation is soluble in water or not depends upon the nature of both the colloid and the electrolyte.

B. Reversible Colloids. The reversible hydrosols are in general not very sensitive toward the salts of the alkali metals. Large quantities of these salts are usually necessary to produce precipitation. The reaction is mostly reversible. Toward the salts of the heavy metals these colloids act in a manner similar to that of the irreversible, inasmuch as often exceedingly small quantities are sufficient for precipitation. In all these cases specific effects are manifested that render a further subdivision into classes extremely difficult.

Contrary to their usual behavior, which would place them in the class with the electrolytes, solutions of dyestuffs frequently exhibit a sensitiveness toward electrolytes very similar to that of metal colloids. The precipitates caused by the salts of the alkali metals can be easily returned to the original form just as in the case of suspensions of clay.

In view of the varied behavior of colloids toward electrolytes it seems scarcely possible to classify them according to this property. By studying the reactions of colloids collectively toward specific reagents it might be possible to arrive at a classification that would resemble the division into groups in analytical chemistry. Such a classification, however, would not give a sharp line of distinction between the various groups, because one and the same colloid may exhibit different reactions, depending upon its age and the method of preparation.

Other Classifications

The differences already mentioned between substances of the type of colloidal gold, on the one hand, and egg albumin on the other, have long been recognized. As a consequence many attempts have been made to classify colloids with these differences as a basis. Noyes proposed to distinguish two groups, colloidal suspensions and colloidal solutions. The former he characterized as nonviscous, nongelatinous, and easily precipitated by electrolytes. The latter as viscous, gelatinous, and difficultly precipitable by electrolytes. Such a classification is not suitable because it takes too many characteristics into consideration. There are many colloids that would not come under these headings. For instance Paal's colloidal silver is nonviscous, and precipitated by electrolytes with great difficulty. Such a point of view would often leave one in grave doubt as to which class colloidal oxides, sulfides, and salts belonged. The properties chosen for

this classification would serve to characterize a few extreme members differing widely, but would not be suitable for the large majority of colloidal substances.

Several other names have been suggested from time to time instead of colloidal suspensions. Perrin advocates hydrophobe colloids; Freundlich, lyophobe colloids; Höber and Wo. Ostwald, suspension colloids; von Weimarn, suspensoids, and so on. Instead of Noyes's colloidal solutions, these authors have suggested hydrophiles, lyophiles, emulsion colloids, and emulsoids, respectively. The author cannot agree with a classification on the basis chosen. The number of characteristics has been further increased by certain authors. The designations, suspensions, and emulsions give ideas about the state of aggregation of the finely divided body that often do not correspond to reality. From these considerations colloidal mercury would belong to emulsion colloids; yet its properties determine its place to be among the suspension colloids. Regarded as a finely divided solid substance colloidal gold, protected by a small amount of gelatin, would fall into the class with other suspension colloids. Its property of withstanding the action of electrolytes, and also the fact that it will gelatinize at higher concentrations makes it conform very well to the definition of emulsion colloids.

Disperse Systems

Hydrosols and hydrogels, the discussion of which will occupy the greater part of this book, fall into the class of finely divided substances or disperse systems. The divided substance Wo. Ostwald * designates as the "disperse phase," the medium in which the particles are suspended as the "disperse medium." Some English authors had previously used the terms "internal phase," and "external phase," for disperse phase and disperse medium respectively. The French have used, "granules colloidaux," and "milieu exterieur."

Wo. Ostwald, following the classification of the author, has divided disperse systems into three subdivisions according to the size of the particles.

1. Coarse dispersoids; suspensions and emulsions.
2. Disperse systems that lie between suspensions and crystalloid solutions; colloidal solutions.
3. Molecular and ionic disperse systems; crystalloidal solutions, both electrolytes and nonelectrolytes.

* Wo. Ostwald: Koll.-Zeit., 1, 291–300, 331–341 (1907); Grundriss der Kolloidchemie, 83. Dresden (1909).

He further divides disperse systems into 9 classes according to the state of aggregation of the disperse phase and disperse medium. Some of these classes play a very important rôle.

EXAMPLES

1. $S + S$ (colored sodium chloride, ruby glass).
2. $S + L$ (minerals with enclosed liquid).
3. $S + G$ (minerals with enclosed gas).
4. $L + S$ (suspensions and hydrosols with solid particles).
5. $L + L$ (emulsions and colloidal solutions with liquid particles).
6. $L + G$ (foam).
7. $G + S$ (smoke, cosmic dust).
8. $G + L$ (mist).
9. $G + G$.

S = solid; L = liquid; G = gas.

This classification gives a comprehensive view of a large number of disperse systems and permits an orderly arrangement into groups just as soon as the state of aggregation of the disperse phase is known. No one will doubt that a suspension of kaolin belongs to the class $L + S$; an oil emulsion to $L + L$; a low hanging rain cloud in the tropics to $G + L$. Difficulties present themselves, however, just as soon as the determination of the state of aggregation of the disperse phase becomes doubtful or impossible. Classification according to this plan becomes merely arbitrary. We must therefore discard in this book any classification that involves the form of the disperse phase.

It will be seen that the effect of Ostwald's classification of colloidal chemistry is to stimulate research for methods of determining the state of aggregation of the finely divided substances. The principles of this classification may be employed, however, as far as they are applicable. This is the case if we consider only three instead of Ostwald's nine classes.

Disperse systems with:

a. A gas as disperse medium.
b. A liquid as disperse medium.
c. A solid as disperse medium.

Just as soon as the state of aggregation of the disperse phase is known Ostwald's classification may be further employed without hesitation.

A few examples of disperse systems with a gas or a solid disperse medium will now be taken up.

Disperse Systems with Gas as Disperse Medium

Disperse systems with air as the disperse medium and water as the disperse phase, such as mist or rain, are of great importance for meteorology and agriculture; while finer subdivisions of water are involved in the blue color of the heavens.

As disperse systems with solid disperse phase may be cited snow clouds, smoke, cosmic dust, and volcanic ashes. The latter are often so fine that they may be carried hundreds of miles by the wind, and become the cause of striking and beautiful color displays in the heavens. Not infrequently has it destroyed large tracts of land, and cities with their inhabitants. Herculaneum and Pompeii fell victims to a rain of ashes; while St. Pierre was destroyed by a "nuée ardente," a hot heavy cloud composed of air, steam, small stones, sand, and dust. The dust was in such a state of fine division that it fell to the ground during the descent of the cloud.*

In other cases on record where the concentration of the dust was not so high the cloud rose and spread itself out in thin layers, forming strange and wonderful forms. Without doubt the dust particles are charged electrolytically and for this reason are prevented from uniting. If during thunder storms the particles become discharged they unite together and fall in showers of ashes. The history of the volcanic eruptions of Mount Vesuvius affords many examples of this phenomenon.

The origin of this dust and the clouds of ashes may very well be explained on the grounds that water vapor in the interior of the volcano at a high temperature and under an enormous pressure is dissolved in the silicates, or forms a sol with them. When the pressure is suddenly released explosions occur owing to the expansion of the enclosed water. The silicates would thus be blown to pieces, a large portion of which would become dust and form a disperse phase in water vapor as a medium. This dust mixed with some moisture might then be precipitated as "nuée ardente," or might fall in a comparatively dry state as ashes. Barus † has shown how such solutions of colloidal silicates may originate. Soft glass, such as is used for glass tubing, swells in water at high temperature and pressure similar to the manner in which gelatin does under ordinary conditions. If now the temperature is sufficiently raised the jelly-like mass melts to a liquid. On cooling under pressure the liquid hardens and becomes a brittle amorphous glass, "waterglass." On heating under atmospheric pressure this mass swells and resembles

* Lacroix: La montagne Pelée et ses éruptions. Paris (1904), Masson et Cie.
† C. Barus: Amer. Journ. of Sc. (4), **9**, 161–175 (1900).

foam. These are the conditions necessary for the origin of "nuée ardente" as well as the masses of pumice stone that are often thrown out from volcanoes.

Disperse Systems with a Liquid as Disperse Medium

In the category of disperse systems with a liquid medium colloidal solutions must be included, especially hydrosols and hydrogels with water as the disperse medium. A great many other liquids may serve as a disperse medium. In point of fact nonaqueous colloidal solutions have assumed a very great importance in the industries. Solutions of gums, rubber, and guttapercha are examples of these. Their thorough *investigation will doubtless form a not unimportant contribution to the chemistry of colloids. Considerable work * has already been done* along these lines that, owing to lack of space, cannot be taken up at this point.

Disperse Systems with a Solid as Disperse Medium

Among the systems with a solid for the disperse medium several are of importance and have been investigated. Only two of them, ruby glass and hardened pyrosols, will be taken up here. Many colored minerals also belong to this class. A thorough investigation with the ultramicroscope would perchance reveal how much more frequent discontinuity is than scientists have been inclined to believe. Even crystals that have always been regarded as homogeneous turn out very often to be discontinuous.

Ruby glass is obtained by melting suitable glass with gold, silver, copper, or with compounds of these metals. The most thoroughly studied is gold glass, which has played an important part in the development of ultramicroscopical methods.† Gold ruby glass can be made by melting lead or barite glass and adding a very small amount of gold chloride. If the glass is quickly cooled it is usually colorless, but becomes colored if slowly reheated. The colorless glass must be considered as a solution of metallic gold in the silicate mass, and not as a chemical combination of gold. By slow cooling, or better still, by careful reheating numberless submicrons of metallic gold are formed in the mass, and these give rise to the color. Their diameter corresponds to that of the particles in a colloidal gold solution. Both submicrons and amicrons are present; the smallest visible with the ultramicroscope

* Koll.-Zeit., **1**, 33–65 (1906–7) von C. O. Weber; 165 von R. Ditmar; 4, 74 (1909) von D. Spencer; **5**, 31 (1909) von H. W. Woudstra; **6**, 136 (1910) von Wo. Ostwald, 202 von F. Hinrichsen u. E. Kindscher, 281 von B. Bysow u. a. m.

† H. Siedentopf und R. Zsigmondy: Drudes Annalen d. Phys. (4), **10**, 1–39 (1903).

have a mass of about 10^{-15} mg. A theory for the formation of ruby glass has been published by the author employing as a basis the fundamental principles of glass formation by Tammann.*

Colored Sodium Chloride. — Siedentopf† has shown that colored sodium chloride, which can be obtained by heating in vacuum in the presence of sodium vapor, is filled with ultramicrons. These have the appearance and show all the properties of a finely divided metal. Precisely as in the case of ruby glass, the color of sodium chloride changes with the temperature. These color variations are attributed to changes in the metallic submicrons. Concerning the polarization of submicrons, see Chapter V.

Pyrosols. — R. Lorenz ‡ defines pyrosols as colloidal solutions of *metals and other substances in a red hot liquid medium. Colloidal metal solutions in fused salts have been correctly recognized and closely* studied. They play an important part in the electrolysis of fused salts, and their presence explains some of the anomalous yields obtained during the decomposition of fusions by the electric current.

The easiest method of preparing pyrosols is by dissolution of the metal in the fused salt, *e.g.*, zinc in zinc chloride, cadmium in cadmium chloride. During the reaction at suitable temperatures sometimes slight explosions take place, whereby the metals give off colored vapor. These phenomena have nothing whatever to do with the formation of subhalides, as has been shown by Lorenz.§ The formation of pyrosols is connected with the increase of the vapor pressure with the temperature. When the vapor tension of the metal is appreciable, the formation of the color is more pronounced. On cooling some pyrosols are permeated with lustrous particles. The intensive color of the mass, and the fact that the color may be destroyed by salting out the pyrosol with sodium or potassium chloride, are evidences that the metal is present in a colloidal state. The homogeneous appearance bespeaks the very fine state of division. Lorenz has thrown light on the relation of pyrosols to ruby glass.

Classification Employed in this Book

Various considerations have actuated the author to choose for the special part of this work, a classification differing from any yet suggested. For the sake of comprehensiveness the special colloids to be

* R. Zsigmondy: Zur Erkenntnis der Kolloide, 128–135.

† N. Siedentopf: Verh. d. Deutsch. Phys. Ges., **7**, 268–286 (1905).

‡ R. Lorenz: Elektrolyse geschmolzener Salze. Halle (1905). II. Teil, 40. — van Bemmelen-Gedenkboek, 395–398 (1910).

§ R. Lorenz: l. c.

taken up are placed in the following groups. The discussion is confined almost exclusively to hydrosols and hydrogels because of their preeminent importance, while organosols and pyrosols have been relegated to a subordinate place.

I. Inorganic Colloids

A. Metals:
  1. Pure metal hydrosols.
  2. Metal colloids with protective colloids.

B. Other elements (S, Se, etc.).

C. Oxides.

D. Sulfides.

E. Salts.

II. Organic Colloids

A. Organic salts.
  1. Soaps.
  2. Dyestuffs.

B. Protein bodies.

As examples especial mention is made of albumin, globin, gelatin, hemoglobin, casein. To these might be added carbohydrates, such as cellulose, starch, dextrin, etc.; also colloids that are soluble in an organic medium, such as resins, rubber, etc. To the inorganic colloids ruby glass and pyrosols must be added.

Because it has been possible, following out the plan of this book, to choose specific colloids so typical of the class to which they belong that they suffice to bring out all the important chemical relations involved in colloidal chemistry, the other members have been largely disregarded. The author has made it a fundamental principle to take up only those colloids the properties of which are known to him through his own investigations.

CHAPTER III

PROPERTIES OF COLLOIDS

Diffusion and Osmotic Pressure

DIRECT measurements of diffusion of hydrosols were made by Graham * and later by Arrhenius † and Herzog.‡ The diffusion constants, D, expressed as $\frac{\text{cm.}}{\text{sec.}} \times 10^5$, are generally very small. For instance, D for egg albumin is 0.052. This would correspond to a molecular weight of 20,000.

The determination of the lowering of the freezing point or the raising of the boiling point gives results with colloids much too inaccurate to be of any use. The measurement of the osmotic pressure has not only the advantage of greater delicacy, but by this method the harmful influences of crystalloidal impurities may be greatly reduced if not completely eliminated. The results obtained with suitable membranes by Pfeffer,§ Rodewald and Kattein,¶ Duclaux,|| Moore and Roaf,** Lillie,†† Biltz,‡‡ and others will be taken up later. Many colloids, of which colloidal iron oxide is an example, give a very considerable rise in the column, while others cause little change. In most cases the osmotic pressure changes with the concentration, but the law governing this change has not yet been discovered. The dependence of the osmotic pressure upon the temperature has been remarked by Duclaux and also by the author in the case of colloidal iron oxide. It is hoped that further work in this field will add to our knowledge of specific hydrosols.

* Th. Graham: Phil. Transact., 183 (1861); Liebigs Annalen, **121,** 13 (1862).

† Sv. Arrhenius: Immunochemie, 17 (1907).

‡ R. O. Herzog: Zeit. f. Elektrochemie, **13,** 533–9 (1907).

§ W. Pfeffer: Osmotische Untersuchungen. Leipzig (1877).

¶ H. Rodewald und A. Kattein: Zeit. f. Phys. Chemie, **33,** 579–592 (1900).

|| J. Duclaux: Compt. rend., **140,** 1468, 1544–1547 (1905); Journ. de chim. phys., **5,** 29–56 (1907).

** B. Moore and H. E. Roaf: Biochemical Journ., **2,** 34 (1906); **3,** 55 (1907).

†† R. S. Lillie: Amer. Journ. of Physiol., **20,** 127–169 (1907).

‡‡ W. Biltz und A. v. Vegesack: Zeit. f. phys. Chemie, **68,** 357–382 (1909); **73,** 481–512 (1910).

Dialysis and Ultrafiltration

The property of plant, animal or artificial membranes to prevent colloids from passing through them has made two very important methods of separation possible. The first one, dialysis, which Graham used with such *notable* results, has already been spoken of. A few other methods of employing this process are described below. The second, ultrafiltration, has in the last few years come into general use in colloidal chemistry. It has already yielded very important results and with further investigation should prove almost indispensable in this field.

Apparatus for Dialysis. Beside Graham's dialyzer, already described on page 7, several others are in use. Generally a membrane is stretched across an open vessel and the whole partially submerged in a larger vessel filled with distilled water as in Fig. 4. If continuous dialysis is desired water is conducted into the outer vessel and out again by means of suitably bent tubing. If no dialyzer is at hand the process may be carried out by means of a bag of parchment membrane pressed into the water and filled with the solution to be dialyzed. Kuehne's dialyzer, Fig. 5, consists of a high glass cylinder which serves to receive the membrane. This latter is a U-shaped tube made of parchment membrane. The funnel and the side tube serve to keep the water renewed. Unfortunately the parchment tubes on the market are so thin that the employment of this sort of dialyzer is rendered difficult. Finally Schleicher and Schüll have used a dialyzer that consists of a parchment tube closed at one end. A dialyzer has been employed in the sugar industry for a long time for the filtration of molasses. Jordis * has constructed a similar apparatus on a small scale.

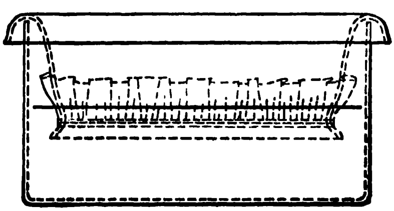


FIG. 4. Dialyzer.

A dialyzer that permits a very rapid purification of the colloid has been described by Zsigmondy and Heyer,† of which Fig. 6 is a diagram. A plate of hard rubber shaped like a crystallizing dish, having a diameter of about 25 to 40 cm. and sides 3 to 4 mm.

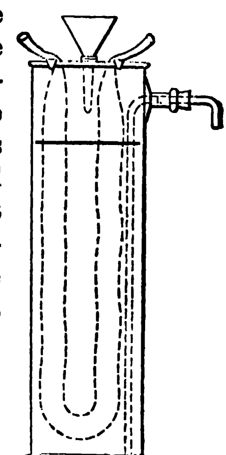


FIG. 5. Dialyzer according to Kühne.

* E. Jordis: Zeit. f. Elektrochemie, 8, 677–678 (1902).

† R. Zsigmondy und R. Heyer: Zeit. f. anorg. Chemie, 68, 169–187 (1910); Koll.-Zeit., 8, 123–126 (1911).

high, is bored through in the center. Eight small strips, 3 to 4 mm. high, are placed radially on the plate and reach to within 1 cm. of the outer edge. These serve to direct the stream of water from the center outwards. A ring of hard rubber (*B*) about 40 mm. high sits exactly upon the edges of plate. The membrane is stretched across the under edge of the ring. By means of this arrangement a layer of water 3 to 4 mm. deep is enclosed between the membrane and the plate. The water is continuously renewed through the hole in the center of the plate, directed toward the outer edge by the strips and flows off through small holes in the upper edge of the plate. It is rather difficult to place the plate quite level and the water is therefore inclined to flow faster through some of the holes than through others. To avoid this strips of filter paper are clamped between the edges of the plate and the bottom of the ring. These strips operate as syphons for the water. Ordinary parchment paper is used as a membrane and has proved itself quite durable. It has the disadvantage of offering considerable resistance to the passage of crystalloids. Of late the so-called fish bladder membranes have been found very suitable for rapid dialysis. They are to be had of fairly good quality on the market. Recently collodion membranes which can be made in any desired form have been employed for the dialysis of colloids with excellent results. The rapidity with which they allow the process of dialysis to take place can be shown in a lecture experiment. Parchment paper and a membrane of collodion are each allowed to hang in the form of a sack in a vessel filled with water. A fairly concentrated solution of fluorescein is poured on each membrane. In a short time the fluorescein will pass through the collodion membrane and fall in beautiful ribbon-like streams to the bottom, while a considerable time will elapse before the same phenomenon will be apparent in the vessel containing the parchment paper.

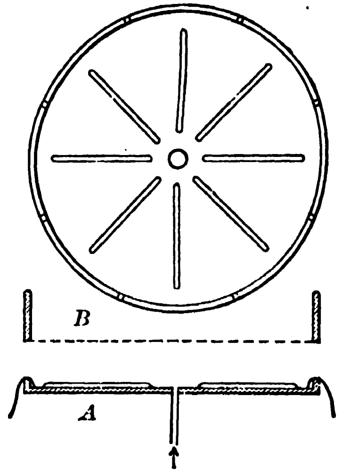


FIG. 6. Cross section of star dialyzer. *A*, plate. *B*, ring with membrane.

Ultrafiltration and Osmometer. Small collodion sacks have been employed for some time by bacteriologists for filtering microbes. G. Malfitano * was the first to point out that these sacks could be used with advantage in the investigation of colloids. The device is now in gen-

* G. Malfitano: Compt. rend., **139**, 1221 (1904).

eral use. Collodion membranes are not only suitable for dialysis, but they also make it possible to separate the colloid from the larger portion of the liquid. It is therefore possible to measure the conductivity of the filtrate and the residue separately. There is the further advantage that these membranes may be employed to determine the osmotic pressure of the hydrosol against its filtrate, and thus enable us to take another step forward in the investigation of colloidal chemistry.

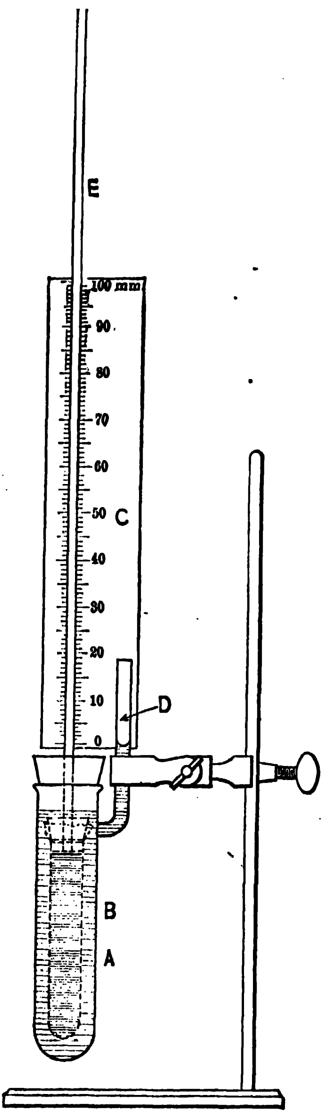


FIG. 7. Osmotic cell.

The preparation of collodion membranes is comparatively simple. According to Malfitano 25 gms. of collodion wool are covered with absolute alcohol and the volume is made up to one liter. The liquid must be prepared some time in advance. A thin film of collodion is formed on the outside of a clean test tube by dipping the latter in the solution. The film is allowed to dry, dipped in water, and the entire process repeated several times in order to obtain a membrane of sufficient thickness. By gentle twisting the membrane may be removed from the test tube and fitted over an open tube having a diameter of the same dimensions as the test tube. The little sack, which looks like the finger of a glove, is filled with water and the latter filtered through by pressure. The sack is thus washed and tested at the same time. A more convenient method is described by Lillie. A concentrated solution of collodion is introduced into a small flask, the excess of which is poured off. The membrane formed on the inside of the walls is now treated with water whereby the film can be easily removed from the glass. The sack is next bound by means of rubber bands to a long tube, the end of which is closed by a rubber stopper.

The membranes are tested by filling them with a colloidal gold solution. The presence of holes or other imperfections is betrayed by the

red color of the filtrate. In the author's laboratory collodion membranes (*B*), Fig. 7, are prepared for osmotic pressure measurements by filling a test tube with the concentrated solution of collodion. For filtration thinner collodion films are desirable. These are prepared by pouring dilute solutions of collodion over glass plates. The solution is made from 200 cc. of a 6 per cent solution of collodion to which is added 200 cc. ether and 500 cc. alcohol. As soon as the films are no longer sticky they are treated with water whereby they are easily loosened from the glass. They are next laid on a piece of paper and placed in a filter funnel. In this form they are suitable for the filtration of either hydrosols or very finely divided precipitates. That they are well adapted for quantitative analysis, such as microanalysis, has been shown by Zsigmondy, Wilke-Doerfurt, and v. Galecki.*

The outer vessel of the osmometer, Fig. 7, has a side tube that is graduated in cubic centimeters. The long tube *E* goes through a rubber stopper into the inner tube. The scale *C* is divided into millimeters and permits the reading of the difference of level in the two tubes. In order to prevent evaporation as far as possible *D* is closed by a rubber stopper through which passes a capillary tube.

Duclaux † has used this apparatus to determine whether there is any change taking place in the colloid. Part of the solution is filtered through a special collodion filter. The remainder of the solution is put into the sack *B* while the filtrate is contained by the outer vessel *A*. If the osmotic pressure is greater in the inner solution the liquid will rise in *E*. After some time the height of the column remains constant. The level is now restored to its former position by means of pressure in *E*. If there has been no change in the colloid the liquid should again rise in the tube until it attains its former maximum. Similar forms of osmometers have been described by Lillie, Hüfner,‡ and by W. Biltz.§

Bechhold's Ultrafiltration. — For the ultrafiltration of colloids in large quantities an apparatus constructed by Bechhold ¶ is well adapted. With this apparatus it is possible to separate colloids from one another according to the size of the pores of the filter. For a filter Bechhold employs strong paper that has been impregnated with hardened gelatin or collodion treated with glacial acetic acid. Accordingly as the solution is dilute or concentrated a filter is obtained with varying permeability. The size of the pores may be varied within certain limits.

* R. Zsigmondy, E. Wilke-Dorfurt und A. v. Galecki, Ber., **45**, 579–582 (1912).

† J. Duclaux: page 33; Journ. de chim., **7**, 430 (1909).

‡ Hüfner: See Chapter XII, page 234.

§ W. Biltz: page 33.

¶ H. Bechhold: Zeit. f. phys. Chemie, **60**, 257–318 (1907); **64**, 328–342 (1908).

The impregnation of the filter is carried out in a special vessel, which permits the treatment of a large number simultaneously. The prepared filters are hardened if necessary and then washed with water.

Fig. 8 is a diagram of Bechhold's apparatus. *P* is a plate that supports the filter funnel *Tr* inside the cylinder *H*. The filter *Fi* is stretched across a piece of wire gauze *N*. Above and below the filter with the gauze suitable calking *G* is arranged. The same material in the form of a ring washer is placed between the edges of the funnel and its lid *D*. The screw ring is for holding the cover securely in place. The solution to be filtered is poured into the funnel and pressure is applied. Comparatively small pressures are necessary for the filtration of colloids. 0.4 atmos. is sufficient to separate the liquid medium from the colloid in the case of dilute hemoglobin solutions. Hemoglobin and serum albumin may be thus concentrated to a greasy paste which will

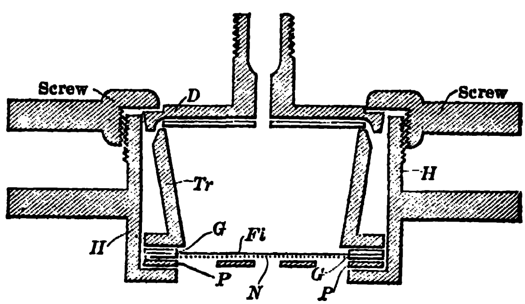


FIG. 8. Bechhold's ultrafiltration apparatus.

redissolve in water. In order to measure the approximate size of the pores in the filter, Bechhold employed a hemoglobin solution. This solution will be retained by the less permeable membranes but will pass through those having large pores. For further information about Bechhold's experiments the original articles must be consulted.

The separation of colloids by ultrafiltration is of very great interest. In this manner Bechhold was able to filter hemoglobin off from a mixture of that colloid in water with Prussian blue. The muddy green mixture gave a red filtrate if a filter with large pores was used, and a colorless filtrate if the filter was more impermeable. Another interesting case is the separation of albumoses. Until this method was discovered the decomposition products of proteids could be separated only by fractional precipitation with salt solutions of different concentrations. See Chapter XII. Bechhold was able by use of filters differing in permeability to separate protalbumoses from deuteroalbumoses, the latter going into the filtrate. It is remarkable that by fractional

precipitation protalbumoses fall out of solution when the concentration of the ammonium sulfate used for that purpose is only one-quarter to one-half the saturation value, while a much stronger solution of ammonium sulfate must be employed in order to coagulate the deuteroalbumoses. Globulin, which requires a certain amount of alkali salts for solution, will coagulate during ultrafiltration into a white opaque mass that redissolves in a solution of sodium chloride.

Very interesting observations with mixtures of colloids and crystalloids have been made by Bechhold. A mixture of colloidal albumin and methylene blue was filtered and the discovery made that the particles of albumin had taken up the methylene blue in a manner similar to the behavior of animal and vegetable tissues. A very pretty experiment illustrates this fact. A solution of methylene blue to which some albumin has been added will not dye wool to the same extent as will a pure solution of the dyestuff alone.

Table 2 contains a list of substances arranged in the order in which they will be retained by filters of decreasing permeability.

TABLE 2

Suspensions	One per cent gelatin solutions
Prussian blue	1 per cent hemoglobin solution (mol. wt. ca. 16,500)
Platinum sols (Bredig)	Serum albumin (mol. wt. 5000 to 15,000)
Colloidal iron oxide	Diphtheria toxin
Casein (in milk)	Protalbumoses
Colloidal arsenious sulfide	Colloidal silicic acid
Colloidal gold solutions No. 4 (about 40 $\mu\mu$)	Lysalbinic acid
Bismon (colloidal bismuth oxide according to Paal)	Deuteroalbumoses (*A*)
Lysargin (colloidal silver according to Paal)	Deuteroalbumoses (*B*). (Mol. wt. ca. 2400)
Kollargol (colloidal silver according to v. Heyden, ca. 20 $\mu\mu$)	Deuteroalbumoses (*C*)
Gold solution * No. 0	Litmus
	Dextrin (mol. wt. ca. 965)
	Crystalloids

It should be noted, however, that this table is arranged with regard to solutions that Bechhold employed and does not necessarily represent the correct relations of the size of particles in colloidal solutions in general. In fact Prussian blue, colloidal iron oxide, and many other colloids may be prepared with particles varying so in size that the relation to hemoglobin would be quite different from that indicated by the table. Finally ultrafiltration is affected not only by the size of the particles, but also by other factors, such as adsorption, electric charge, etc.

* The position of this solution in relation to hemoglobin has not yet been definitely determined.

Movements of the Ultramicrons

One of the characteristic properties of colloidal solutions is the more or less energetic movement of the particles. The closer study of this movement has been made possible by the ultramicroscope. The movement of very small particles can be seen with the ordinary microscope, and has been known since 1827. It was discovered by a botanist, Robert Brown,* and has been named after him. It has since been thoroughly investigated by a large number of scientists. A short bibliography relative to the earlier experiments will be found in Lehmann's Molekularphysik, 1, 264 (1867).

Many theories have been evolved to explain this phenomenon. Regnault † assumed that the heating of the particles on one side more than the others caused small convection currents and this accounted for the vibrating movement of the particles. Wiener ‡ concluded that it was a movement peculiar to the liquid state, imperceptible of itself but rendered manifest by the colloidal particles. According to Quincke § the Brownian movement is due to the spreading out of layers of liquid over the surface of the particles. A really useful theory was first arrived at by the application of the kinetic hypothesis. Wiener, Cantoni, Renard, Boussinesq, and Gouy have all explained the movement on the grounds of collisions between the particles and the molecules of the liquid. It remained, however, for the theoretical considerations of Einstein ¶ and v. Smoluchowski || to point out the way in which the experimental proof could be obtained. The proof has been given by The Svedberg,** Ehrenhaft,†† Perrin,‡‡ and argues for the justification of the application of the kinetic theory.

Many observations had already shown the fallacies in the older theories. For instance it had been shown that the Brownian movement

* R. Brown: Poggendorffs Annalen d. Phys. u. Chem., **14**, 294–313 (1828).

† J. Regnault: Journ. de Pharm. (3), **34**, 141 (1858).

‡ Chr. Wiener: Poggendorffs Annalen d. Phys. u. Chem., **118**, 79–94 (1863).

§ G. Quincke: Verh. d. Ges. D. Naturf. u. Ärzte. Düsseldorf, 26–29 (1898); Beibl. z. d. Annalen de Phys. u. Chem., **23**, 934–937 (1899).

¶ A. Einstein: Drudes Annalen d. Phys. (4), **17**, 549–560 (1905); **19**, 371–381 (1906); Zeit. f. Elektrochemie, **14**, 235–239 (1908).

|| M. v. Smoluchowski: Drudes Annalen d. Phys. (4), **21**, 756–780(1906); **25**, 205–226 (1908).

** The. Svedberg: Studien zur Lehre von den kolloiden Lösungen, 125–160. Upsala (1907).

†† F. Ehrenhaft: Sitzungengsber. d. Akad. d. Wiss. Wien, **116**, IIa, 1139–1149 (1907).

‡‡ J. Perrin: Annales de Chim. et de Phys. (8), **18**, 5–114 (1909). J. Donau: Kolloidchem. Beihefte, **1**, 1–258 (1910).

was independent of external influences. A good suspension of rubber can be boiled for a week at a time, and if cooled there will be no change in the Brownian movement. The heat rays, any specific color, or all the colors may be cut off; or the intensity of the illumination may be varied a thousand-fold without changing the movement in the slightest. From this it may be concluded that the cause is not local changes of temperature, as has been claimed by many scientists, but is a permanent phenomenon independent of exterior circumstances.

Investigations with the ultramicroscope * have established the following facts: —

1. The Brownian movement is inversely proportional to the size of the particles. In fact with particles of very small dimensions the movements may become so violent as to assume, from all appearances, an entirely different character.*

2. The movement is independent of the heat rays; these are cut off entirely before the ray passes into the cuvette of the ultramicroscope.

3. The movement is not caused by evaporation because the observations were made in a closed vessel completely filled with the liquid.

4. The movement is independent of the direction of the rays, of the intensity of the illumination, and of its duration.

5. The particles appear to affect one another, as the movement is somewhat less energetic when the solution is diluted.

Theory of the Motion.—The theory of Einstein † (v. Smoluchowski ‡ came independently to the same result) assumes no difference between true molecules and particles suspended in the same medium. The particles behave as if they were true gas molecules with normal kinetic energy but a much shorter free path. The following is the Einstein formula.

$$A = \sqrt{t}\sqrt{\frac{RT}{N} \cdot \frac{1}{3\pi\eta r}},$$

where

A is the amplitude (in the direction of the x axis),
t is the corresponding time,
R is the ordinary gas constant,
T is the absolute temperature,
N is the number of molecules in one gram mol,
η is the viscosity of the medium,
r is the radius of the particles (average).

v. Smoluchowski from quite other assumptions came to the same formula except that another integer is introduced.

* R. Zsigmondy: Zur Erkenntnis der Kolloide, 106–111 (1905).
† l. c. ‡ l. c.

The experimental proof of the formula is possible from several directions.

1. It is possible to determine how the amplitude changes with the temperature. This has been recently done by Seddig * working with solutions of tin.

2. It is also possible to determine how A changes with the size of the particles.

Svedberg † investigated the formula by two other methods. He determined whether or not the amplitude measured agreed with that calculated from the formula. By a suitable contrivance on the ultramicroscope he was able to resolve the irregular vibratory motion into waves. By measuring the wave length, the amplitude and the rate of flow of the liquid through the cuvette he found the time. The values thus obtained are somewhat larger than those calculated. It is probable that wave length was underrated where the amplitude was large.

Svedberg also succeeded in confirming the relations represented by following formula:

$$\frac{A^2\eta}{t} = \text{const.}$$

It will be readily seen that this formula comes directly from the original one if T and r are kept constant.

Of importance is the conclusion arrived at by experimental methods that the Brownian movement is independent of the electric charge. The claim that the motion is due to an interchange of charges between ions and the particles is therefore untenable.

Very important in relation to the motion of larger particles are the researches of Perrin ‡ on gamboge and mastic solutions. They show that the spontaneous sedimentation under the influence of gravity is governed by the same laws that obtain in regard to the molecules of the atmosphere. Just as the density of the gas changes with the height according to an exponential law, so does the density of the particles in suspension change with the depth of the medium. For gases the concentration becomes one-half for every $3\frac{3}{4}$ miles increase in height; while in the case of suspended particles the distance is only $\frac{1}{10}$ mm. for the same change in concentration. Perrin was enabled by his results to calculate the kinetic energy of a single particle, and found it to correspond to that of a molecule. By measuring the change of place of the particles every 30 seconds Perrin was able to show the validity

* M. Seddig: Habilitationsschr. d. Akad. Frankfurt a. M. (1907); Zeit. f. anorg. Chemie, 73, 360–384 (1912).

† Svedberg: l. c.

‡ Perrin: l. c.

of Einstein's formula. For further information reference must be made to the original article. Also see Mecklenburg.* A recent article by Svedberg and K. Inouye † has shown that the formula of Einstein is applicable in the case of colloidal gold solutions. The value of N determined, 6.2×10^{23}, agrees exactly with that given by Rutherford, and very well with Perrin's, 7.1×10^{23}.

The most important results may be summed up as follows. Suspended particles have the same kinetic energy as gas molecules. The particles exert an osmotic pressure on a membrane impermeable to them. This osmotic pressure is dependent upon the temperature and upon the number of particles in the unit volume. The last named fact applies to particles of all sizes. While the osmotic pressure is too small for measurement in colloidal suspensions, it is much greater than the experimental error in the case of hydrosols where the particles are very small, and can therefore be determined with some degree of accuracy.

Osmotic Pressure and the Number of Particles

It has been repeatedly proved experimentally that the osmotic pressure of a colloidal solution is proportional to the number of particles. In case the colloid is free from electrolytes we have, therefore, another means of determining the number of particles. The properties of a colloidal solution change gradually with a decrease in the number of particles. Amicrons unite with each other to form submicrons and finally the entire colloid coagulates. If such an occurrence is followed in an osmometer the pressure sinks to zero during the coagulation, or quite often before it takes place. Many colloids are very stable and manifest the same osmotic pressure for months. Under the ultramicroscope these show no change in the particles.

The influence of electrolytes on albumin and gelatin has been determined by Lillie.‡ The concentration of the electrolyte was made the same in both the outer and the inner liquids. The hundreds of experiments that he carried out all go to show that electrolytes having a precipitating effect on the colloid diminish the osmotic pressure. In cases, on the other hand, where the electrolyte causes swelling or distention, and subsequent dissolution of the colloid, the osmotic pressure is increased. The law of Hofmeister and Paal was confirmed, which states that salts having an intense precipitating effect

* W. Mecklenburg: Die experimentelle Grundlegung der Atomistik. Jena (1910).

† The Svedberg und K. Inouye: Arkiv. for kemi, mineral. och geol. 4, No. 19; Zeit. f. phys. Chemie, 73, 547–556 (1910).

‡ Lillie: l. c.

diminish the osmotic pressure more than do those which cause little precipitation.

The dependence of the osmotic pressure upon the temperature is of interest. But here the same law obtains, namely that any circumstances causing the particles to unite diminish the pressure. With colloidal iron oxide a rise of temperature lessens the osmotic pressure. With many other colloidal substances, such as gelatin, raising the temperature increases the number of particles and therefore the osmotic pressure becomes greater.

From the evidence we have, showing that the osmotic pressure varies *with the size of the particles, we may conclude that colloidal particles* cause the pressure. It is undeniable, of course, that any electrolyte present as impurity will increase the values obtained by measurement.

Electrical Properties of Colloids

Under the influence of a fall of potential almost all colloids migrate either to the cathode or to the anode. The phenomenon of electrical migration of colloids is closely associated with that of electro-osmosis. This latter phenomenon may be defined as the passage of liquids through membranes under the influence of a fall of electrical potential. When the particles move through the solution the phenomenon is called cataphoresis. When the particles remain stationary and the liquid moves, the term endosmosis is applied. The earliest observations on these phenomena were made by Picton and Linder,* Coehn,† Lottermoser,‡ and Wiedemann.§

Suspended particles in contact with a liquid medium take on a charge either positive or negative, as has been shown by Quincke.¶ These charges determine the direction in which the particles will travel in the current. With regard to the nature of the charge, a law enunciated by Coehn ‖ gives us information. Substances with a high dielectric constant become charged positively toward those with a lower. The dielectric constant of water is 80, which is very high, and therefore most colloids are charged negatively in pure water; in other words the particles move towards the anode. On the other hand the dielectric constant of turpentine is low, therefore the particles suspended in it

* H. Picton and S. E. Linder: Journ. Chem. Soc., **61**, 148–172 (1892).

† A. Coehn: Zeit. f. Elektrochemie, **4**, 63–67 (1897).

‡ A. Lottermoser und E. v. Meyer: Journ. f. prakt. Chemie (2), **56**, 241–247 (1897).

§ G. Wiedemann: Poggendorffs Annalen d. Phys. u. Chem. **87**, 321–352 (1852). Die Lehre von der Elektrizität, (2 Aufl.), 1, 993–1019 (1893).

¶ G. Quincke: Poggendorffs Annalen d. Phys. u. Chem., **113**, 513–598 (1861).

‖ A. Coehn: Wiedemanns Annalen d. Phys. (N. F.), **64**, 217–232 (1898).

assume a positive charge and move toward the cathode. The law obtains quantitatively only for substances having a very low conductivity. Coehn and Raydt * found that dielectric constants could be calculated from the height of the electro-osmotic column.

The influence of the presence of electrolytes is of first importance in the nature of the charge on the particles. The adsorption of ions and other chemical reactions are deciding factors. The following table shows the charges that are usually found on colloidal particles, provided that the customary methods of preparation are employed, and the colloids purified by dialysis. Under special circumstances the charges may be just the opposite of that given in the table.

TABLE 3

Migration toward cathode +	*Charge of the Particles*
Colloidal iron oxide	Colloidal gold, silver, platinum
" cadmium hydroxide	" sulfur
" aluminium hydroxide	" arsenious sulfide
" chromium oxide	" antimonious sulfide
" titanic acid	" cupric sulfide
" thorium oxide	" lead sulfide
" zirconium oxide	" cadmium sulfide
" cerium oxide	" mastic
Basic dyestuffs, dissolved either as a colloid or a crystalloid	" gamboge, gum arabic
	" soluble starch
	" silicic acid
	" stannic acid
	" molybdenum blue
	" tungsten blue
	" vanadium pentoxide
	Acid dyestuffs (colloidal as well as crystalloidal)

The hydrogen and hydroxide ions are especially effective in determining the nature of the charge. Hardy † found that albumin had no perceptible charge in pure water, but that traces of alkalies or acids caused the albumin to go to the anode or to the cathode respectively. Perrin ‡ found the same rule to hold for many suspended powders, and many hydrosols, such as albumin solutions. Pauli § corroborated Perrin's results on proteids.

A remarkable fact was discovered by Coehn, ¶ namely that crystal-

* A. Coehn und U. Raydt: Annalen d. Phys. (4), **30**, 777–804 (1909).

† W. B. Hardy: Journ. of Physiol., **24**, 288–304 (1899); Zeit. f. phys. Chemie, **33**, 385–400 (1900).

‡ J. Perrin: Compt. rend., **136**, 1388–1391 (1903); **137**, 513–547, 564–566 (1903).

§ W. Pauli: Hofmeisters Beiträge z. chem. Phys. u. Path., **7**, 531–547 (1906).

¶ A. Coehn: Zeit. f. Elektrochemie, **15**, 652–654 (1909).

loidal solutions of non-electrolytes, such as sugar, migrate toward the anode in dilute alkali and toward the cathode in dilute acid solution.

The above laws are not of general application, however. Many colloids refuse to change their direction with the nature of the solution. To this class belongs silicic acid which always migrates toward the anode unless a concentrated acid solution is employed.

Although there exists a very great similarity between the behavior *of colloids and suspended particles in the electric current it should not be overlooked that the former manifest an even greater similarity to* the migration of ions. True suspensions may be discharged at both poles, so that colloids seem to occupy a position intermediate between suspensions and crystalloids.

Endeavors to determine the electrochemical equivalent of colloids have not been very successful in most cases owing to the confused relations between the size of the particles and the charge. Sometimes it is quite impossible because the substance is partly colloid and partly crystalloid, *e.g.*, Benzopurpurin, Congo red. Nevertheless, the amount of electricity on a definite amount of colloid has been determined. In all cases, however, where the particles migrate and are discharged at the electrodes, electricity must be transported. Although it is very small in comparison to that of solutions of electrolytes, owing to the comparatively small number of particles involved, it has been often determined in the case of hydrosols.

The rate of migration of colloidal particles is of the same order as that of suspensions and ions. This will be apparent from the following table, which gives the rate in μ per second for a potential fall of one volt per centimeter.

TABLE 4

	$\frac{\mu}{\text{Sec.}}$
Particles having a diameter of 35 μ	2.5 Quincke
Colloidal silver	2.0 Svedberg
" "	2.0 Burton
" " (direct current)	3.2–3.8 Cotton and Mouton
" " (alternating current)	3.8 Cotton and Mouton
Colloidal gold (average)	4.0 v. Galecki *
Anion of butyric acid	3.1 Ostwald, Bredig
Limit of mobility of organic ions having a high molecular weight	ca. 2.0
H^+	32.9
OH^-	18.0
Cl^-	6.8

* A. v. Galecki: Zeit f. anorgan. Chemie, 74, 174–206 (1912).

The electrolysis of stannic acid hydrosol, or the purple of Cassius takes place in precisely the same manner as that of the crystalloids, methyl-orange, or the sodium salts of dyestuffs. In both cases under the microscope the separation of the alkali soluble constituent may be seen at the cathode. Where the particles are small enough no movement can be perceived even under the ultramicroscope. Determinations of the migration numbers have shown that in one case seven and in others ten gram mols of stannic acid were transported for every equivalent *of silver deposited in the voltmeter. A portion of the stannic acid* was deposited on the anode.

The migration of colloids frequently differs from that of electrolytes, in that coagulation may occur before the electrode is reached, as in the case of colloidal gold protected by gelatin;* or the colloid may migrate toward one electrode and then change its direction; some albumins and many colloidal metals show this disposition. The cause is doubtless due to the fact that the cathode portion becomes alkaline, the anode acid during the electrolysis. The translator has remarked this behavior on the part of many colloids. Finally colloids are unable to penetrate parchment paper even with the help of the current, becoming discharged and coagulating instead.† Analogous observations have been made during ordinary electrolysis.‡ From Table 4 it is apparent that the rate of migration is independent of the size of the particles.

Apparatus for the Determination of the Direction of Migration. — The direction and the rate of migration of ultramicrons may be determined either macroscopically or ultramicroscopically. The U-shaped tube, Fig. 9, used by Coehn,§ lends itself very well for macroscopic observations. The two stopcocks have a bore exactly the size of the diameter of the remainder of the tube. The apparatus is filled with the colloidal solution and the cocks are closed. The two end portions are then rinsed out, filled with water, and the electrodes introduced into them. The cocks are next opened and the current turned on. In a very short time it will be seen that the boundary between the colloidal solution and the water is moving either toward the cathode or

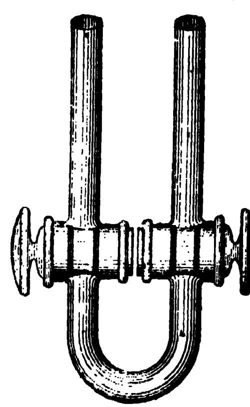


FIG. 9. Coehn's apparatus.

* J. Billitzer: Zeit. f. Elektrochemie, **8**, 638–642 (1902); Zeit. f. phys. Chemie, **45**, 307–330 (1903).

† R. Zsigmondy: Liebigs Annalen, **301**, 36 (1898).

‡ W. Ostwald: Zeit. f. phys. Chemie, **6**, 71–82 (1890).

§ A. Coehn: Zeit. f. Elektrochemie, **15**, 653 (1909).

toward the anode.* In the case of ultramicrons, easily seen in the ultramicroscope, the progress of the individual particles may be followed by means of this instrument. Cotton and Mouton * have described an apparatus for this purpose, and given directions for its use. A somewhat different apparatus has been constructed by Svedberg † by which he was able to make a very interesting study of the relation of charge to motion of the individual particles.

Charge on the Particles. — There is no longer any doubt as to the existence of a charge on the particles, and it therefore behooves us to consider the origin of these charges. In the case of electrolytes the assumption is made that the molecule dissociates into a positive and a negative ion. That holds for simple salts or for those where the ions may be complex and have a high molecular weight. If these complex ions were increased in mass until the molecular weight is several thousand, the solution would have colloidal properties. This is doubtless the way in which the electric charge originates in special cases; for instance, dyestuffs with high molecular weights. The phenomenon would then be quite analogous to that of the formation of ions. In a large number of cases, however, this explanation would meet with difficulties. When non-conductors are under consideration the charge may be explained by the difference in the dielectric constant of the disperse phase and the disperse medium, as already mentioned on page 44. In other cases the existence of the charge must be explained on the assumption of the adsorption of ions, or the giving off of ions to the liquid. Suppose we take for example colloidal cadmium made by Bredig's method. The individual cadmium particles would be tiny electrodes, sending off positively charged ions, and becoming themselves charged negatively. Doubtless the conductivity of this solution would be greater than that of water, and both the charged particles and the ions would take part in the transportation of electricity. The amount carried by each of these two factors would depend upon the number of individuals, the charge, and the rate of migration. If such a solution were electrolized cadmium should be deposited on both electrodes. More would be found on the anode than on the cathode, because the mass of the colloidal particles is much greater per unit charge than that of the ions. This could probably not be carried out in practice because these metals with a high solution tension would oxidize rapidly, and the oxides generally travel in the opposite direction to that of the particles of pure metal.

The electric charge may be explained in the case of royal metals also

* A. Cotton et H. Mouton: Les ultramicroscopes, etc., 144. Paris (1906).

† The. Svedberg: Studien zur Lehre von den kolloiden Lösungen, 149. Upsala (1907).

by the adsorption or dissociation of ions. During Bredig's process the colloidation takes place principally at the cathode, where hydrogen is copiously discharged. The metal particles may contain a great deal of free hydrogen, give off hydrogen ion, and become negatively charged, just as occurs when a hydrogen electrode is placed in water. This assumption has been made by Billitzer. The acquisition of a charge by gels through peptisation will be taken up in Chapter IV. It can be explained only by adsorption.

The fundamentals of the electrical theory of irreversible colloids have been dealt with by Hardy.* To him belongs the credit of having made clear the relation between the nature of the charge and the precipitation of colloids by electrolytes. According to his theory it is the electric charge on the particles of irreversible colloids that determines the stability. If the charge is neutralized by the addition of electrolytes, the isoelectric point is reached and the particles unite; or, in other words, coagulation occurs. That colloids sensitive to electrolytes do coagulate in the neighborhood of the isoelectric point has been repeatedly shown. Such ions may take part in the coagulation which have a charge opposite to that of the colloidal particles. This theory has thrown light on a great many previously unexplained relations. It was not difficult to see that the origin of the charge on the particles was due either to a specific partition coefficient between the particles and the medium,† to the dissociation of ions by the particles,‡ or to the adsorption of one ion more than the other.§

Discharge of the Particles. — The gradual discharge of the particles may be followed macroscopically (Burton),¶ in a Nernst-Coehn apparatus, or ultramicroscopically according to Svedberg. By the latter method it is possible to show whether the charge has any effect on the Brownian movement or not. Svedberg || elicited that the movement is independent of the presence of a charge. He employed colloidal silver and aluminium sulfate in his work, and found that a few hundred thousandths of one per cent of the sulfate were sufficient to render the silver particles neutral toward the medium. The vibration had an amplitude of 2.2 to 2.25 μ regardless of whether the particles were neutral, charged positively, or negatively. From this it can be at once concluded that the motion is not due to electrical causes.

* Hardy: l. c.

† G. Bredig: Anorganische Fermente, 16. Stuttgart (1901).

‡ J. Billitzer: l. c.

§ Zsigmondy: Zur Erkenntnis der Kolloide, page 165–169.

¶ E. F. Burton: Philos. Magazine (6), **11**, 425–447 (1906); **12**, 472–478 (1906); **17**, 583–597 (1909).

|| Svedberg: l. c.

The isoelectric point is known by the fact that the particles unite to form large complexes, and also that they do not move either toward the anode or cathode when a fall of potential exists between the electrodes.

The exact concentration was 60.10^{-8} g. aluminium to 1 g. of the colloid solution. If more aluminium sulfate was added the particles moved in the opposite direction. The gradual discharge of the particles can be seen from the following table. Recently Galecki * has verified the results of Burton and Svedberg.

TABLE 5

Grams of Al^{+++} in 100 cc.	$\frac{\mu}{\text{sec.}}$ for a potential fall of 1 V per cm.	Grams of Al^{+++} in 100 cc.	$\frac{\mu}{\text{sec.}}$ for a potential fall of 1 V per cm.
0	2.0	52.10^{-6}	0.26
Traces	1.38	69.10^{-6}	−0.42
17.10^{-6}	1.29	87.10^{-6}	−0.61
35.10^{-6}	1.03	173.10^{-6}	−1.56

Magnitude of the Charges on the Particles. — In order to explain the coagulation of colloids by electrolytes, Billitzer † assumed that the charge on the particle was small in comparison to that on an ion molecule. One ion molecule should therefore be able to discharge a large number of colloidal particles and cause them to unite. This hypothesis does not, however, agree with the facts. The ultramicroscopical investigation of migration has revealed the fact that the rate of all the particles in a given hydrosol is almost the same, and that every particle is only gradually discharged on the addition of an electrolyte. This would go to show that the charge on an individual particle must be large compared to that on a univalent ion molecule. Were this not the case the addition would cause a sudden change of direction of the particles instead of a gradual diminution of velocity. Another evidence of the truth of this deduction regarding the magnitude of the charge is the fact that the velocity of the particles is about the same as that of ion molecules. As the former are very much larger the charge must be correspondingly greater in order to produce the same velocity.

Assuming Stokes' ‡ formula the magnitude of the charge on a particle of known diameter may be calculated from its velocity. This

* A. v. Galecki: Zeit. f. anorg. Chemie, **74**, 174–206 (1912).

† J. Billitzer: Zeit. f. phys. Chemie, **51**, 129–166 (1905).

‡ Kirchhoff: Vorlesungen über Mechanik., 26 Vorlesung. Leipzig (1897).

sort of calculation indicates that the charge on an individual particle of medium size must be considerable. In Stokes' formula

$$e = \frac{6\,\pi\eta r u}{H}:$$

e is the charge, η the viscosity of the medium, r the radius of the particles, and u the velocity of the particles for the potential fall H. For silver particles $u = 2\frac{\mu}{\text{sec.}}$, $H = \frac{\text{volt}}{\text{cm.}}$, $\eta = 0.0105$, and $r = 25\ \mu\mu$. Substituting these values in the equation we have

$$e = \frac{6 \times 3.14 \times 1.05 \cdot 10^{-2} \times 25 \cdot 10^{-7} \times 20 \cdot 10^{-5}}{\frac{1}{300}} = 297 \cdot 10^{-10}$$

electrostatic units; or 99 elementary quantums, where the value of one quantum is 3.10^{-10} electrostatic units. The charge on a silver particle having a diameter of 50 $\mu\mu$ and a velocity of 2 μ would be equal to that of 99 molecules of chloride ion.*

During the discharge and coagulation of colloids by electrolytes the particles adsorb ions having a charge opposite to their own. The precipitating ion is carried down with the colloid and generally cannot be removed by washing. This ion may, however, be replaced by an equivalent amount of another ion having the same valence. Many examples of this have been observed by Picton and Linder, Spring, Whitney and Ober, and others. Picton and Linder † found that colloidal arsenious sulfide, precipitated by a solution of calcium chloride, carried down some of the calcium and left an equivalent amount of hydrogen ion in solution. In other words the solution became acid. The calcium in the precipitate could be substituted by an equivalent amount of barium. The explanation of this phenomenon will be given in Chapter IV. Spring ‡ made a similar observation with mastic and copper sulfate. Whitney and Ober § carefully investigated the precipitation of arsenious sulfide by the salts of the alkaline earth metals and found that a fixed amount of the hydrosol adsorbed equivalent quantities of these metals ¶ as oxides (or hydroxides) from solutions of their salts.

The table shows that almost equivalent quantities of the metals were adsorbed and carried down. Under the assumption that the amount of the metal found in the precipitate was exactly the quantity necessary

* Freundlich: Kapillarchemie, page 243. Leipzig (1909).

† H. Picton and S. E. Linder: Journ. Chem. Soc., **67**, 63–74 (1895).

‡ W. Spring: Archives des Sc. Phys. et Natur. (4), **10**, 305–321 (1900).

§ W. R. Whitney und J. E. Ober: Zeit. f. phys. Chemie, **39**, 630–634 (1902).

¶ Chapter IV.

to neutralize the charge on the particles, and that nothing was lost during washing, etc., it would be possible to calculate the magnitude of the charge on the individual particles provided the average mass was known. Freundlich * has recently used the precipitation values to determine the valence of ions.

TABLE 6

Grams adsorbed by 100 cc. of the colloidal solution

	Found	Calculated
Ca	0.0019 0.0020	0.0022
Sr	0.0036 0.0041	0.0049
Ba	0.0076	0.0076
K	0.0036	0.0043

Coagulation

The coagulation by electrolytes has been studied mostly with pure colloids of metals or with sulfides. The laws deduced for these special cases are not of general application. These systems are sensitive to the action of electrolytes. The cause for this will be discussed in detail in the chapters on metal colloids. In any case there is a strong tendency in the system for the metal and the water to reach a more stable state and separate from each other. The coagulation of the particles is a spontaneous irreversible reaction requiring a long time for its completion, and a slight aid by the electrolyte causes the rate to increase very greatly. The coagulation may occur during filtration, or centrifugalization, without the presence of the electrolyte. Contrary to the reversible coagulation of clay suspensions that of the metal colloids is quite irreversible. Nevertheless there are points of semblance in the two cases. In each the particles are discharged.

In order to precipitate a given colloid by a certain electrolyte, a minimum concentration must be exceeded. Bodländer † has called this value the Schwellenwert. This minimum is not easily determined because several other factors are involved; such as the rate at which the addition is made, the method of stirring, etc. Freundlich ‡ found that a given volume of electrolyte was sufficient to cause complete precipitation if added quickly; but that the coagulation was only partial if the addition was made very slowly. If the operation is performed

* Zeit. f. phys. Chemie, 80, 564 (1912).

† G. Bodländer: Neues Jahrb. f. Min. Geol. usw., 2, 147–168 (1893).

‡ H. Freundlich: Zeit. f. phys. Chemie, 44, 129–160 (1903).

in the same manner each time, the amounts necessary agree very well with one another.

Rate of Coagulation.—When a sufficiently large excess of the electrolyte is added the rate of coagulation is usually very great. It generally occurs immediately on shaking. On the other hand, sedimentation is in most cases slow. Sometimes coagulation occurs simultaneously with chemical reactions between the colloid and the electrolyte. In such cases astonishing results are often obtained. One would expect, for instance, that colloidal iron oxide and hydrochloric acid would unite to give ferric chloride, without the formation of a precipitate. If the experiment is performed with a somewhat old specimen of the hydrosol a precipitate is at first formed which redissolves to give a solution of ferric chloride. Similarly aqua regia and potassium cyanide cause colloidal gold to change to a violet color although both dissolve finely divided gold. Here, as in the previous case, coagulation occurs more rapidly than the dissolution of the substance. A great many other analogous cases are known in which a precipitate is obtained at first where one would expect immediate dissolution.

Valence Relations.—The comparison of the precipitating values of different electrolytes found by Schulze,* Prost,† Picton and Linder ‡ gave the interesting result that univalent cathions have a less intensive effect than bivalent; and these in turn were not so effective as trivalent cathions. This can be easily seen from Table 7 constructed by Freundlich.§

TABLE 7

A_2S_3 hydrosol, charged negatively, concentration = 1.857 gms. per liter

Electrolyte.	Precipitation value in millemols per liter.	Electrolyte.	Precipitation value in millemols per liter.
$KC_2H_3O_2$	110.0	$MgCl_2$	0.717
$LiCl$	58.4	$MgSO_4$	0.810
$NaCl$	51.0	$CaCl_2$	0.649
KNO_3	50.0	$SrCl_2$	0.635
KCl	49.5	$BaCl_2$	0.691
$\frac{K_2SO_4}{2}$	65.6	$ZnCl\ 2$	0.685
		$UO_2(NO_3)_2$	0.642
NH_4Cl	42.3	$AlCl_3$	0.093
HCl	30.8	$Al(NO_3)_3$	0.095
		$\frac{Ce_2(SO_4)_3}{2}$	0.092

* H. Schulze: Journ. f. prakt. Chemie (2), **25**, 431–452 (1882); **27**, 320–332 (1883).

† E. Prost: Bulletin de l'Acad. Roy. de Belg. (3), **14**, 312–321 (1887).

‡ H. Picton and S. E. Linder: Journ. Chem. Soc., **67**, 63–74 (1895).

§ H. Freundlich: Zeit. f. phys. Chemie, **73**, 385–423 (1910).

By precipitation value is understood that concentration of the salt lying between two other concentrations, the greater of which causes the liquid to become clear, and the smaller of which leaves the liquid slightly turbid.

Picton and Linder * demonstrated that the precipitation of positively charged hydrosols, such as colloidal iron oxide, was similarly affected by the valence of the anion.† See Table 8.

TABLE 8

Fe_2O_3 hydrosol, charged positively, 1.744 gms. $Fe(OH)_3$ per liter

Electrolyte.	Precipitation value mille-mols. per liter.	Electrolyte.	Precipitation value mille-mols. per liter.
KCl	9.03	K_2SO_4	0.204
KNO_3	11.9	$MgSO_4$	0.217
$\frac{BaCl_2}{2}$	9.64	$K_2Cr_2O_7$	0.194

TABLE 9

Electrolyte.	Precipitation value in mille-mols per liter.	Electrolyte.	Precipitation value in mille-mols per liter.
NaCl	51.0	Aniline hydrochloride	2.52
Guanidine nitrate	16.4	Morphine chloride	0.425
Strychnine nitrate	8.0	New fuchsine	0.114

Freundlich ‡ verified these results, and found further that the adsorption of the ions played a part. That is, strongly adsorbed cathions precipitated negatively charged hydrosols, and *vice versa*, adsorption of an anion caused the precipitation of positively charged hydrosols. This will be apparent from Table 9.

It is worthy of note that morphine chloride and fuchsine have an abnormally low precipitation value, although each forms a univalent cathion. Moreover, a great many cathions of the heavy metals have a smaller value than corresponds to their valence, so that this law is somewhat limited in its application.

Freundlich has attempted to explain the law by use of adsorption isotherms, Fig. 10. Under the assumption that the cathions of all light metals are adsorbed to the same degree it follows from the adsorption isotherms, that the precipitation values of univalent ions

* H. Picton and S. E. Linder: Journ. Chem. Soc., **87**, 1906–1936 (1905).

† Exceptions to the rule are given in Chapter VII, Colloidal Iron Oxide.

‡ H. Freundlich: Zeit. f. phys. Chemie, **73**, 385–423 (1910).

must be much larger than those of bivalent or trivalent ions. In order to neutralize the charge on ultramicrons equivalent amounts of cathions must be adsorbed, or expressed in mols, three times as much of potassium as of aluminium ion. The abscissas, Fig. 10, represent the concentration in the solution necessary for precipitation. These relations have been almost quantitatively confirmed by Freundlich.

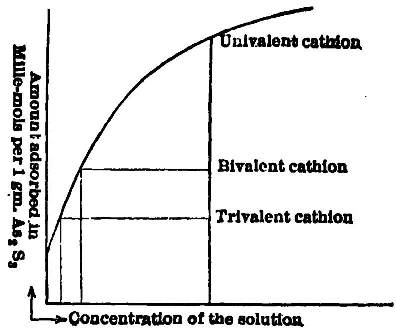


FIG. 10.

As an example of how this law may be made use of, an article by Galecki may be cited. Many investigators have doubted the valence of beryllium. Galecki * determined the precipitation values of different salts on As_2S_3. Table 10 gives the results obtained. It can be seen that beryllium comes in the same category as the bivalent metals.

TABLE 10

20 cc. As_2S_3 76 mille-mols. per liter			
0.01N Ba $(NO_3)_2$	1.85	1.9	1.85 cm.
0.01 $BeSO_4$	1.85	1.8	1.85 "
0.01 Be $(NO_3)_2$	1.85	1.85	1.8 "
0.01 La $(NO_3)_3$	0.15	0.15	0.15 "
0.01 $AlCl_3$	0.1	0.15	0.15 "
20 cc. As_2S_3 150 mille-mols. per liter			
0.01N Ba $(NO_3)_2$	0.9	0.9	0.9 cc.
0.01 Be $(NO_3)_2$	0.95	0.9	0.9 "
0.01 Mg $(NO_3)_2$	0.8	0.9	0.9 "
0.01 La $(NO_3)_3$	0.05	0.05	....

Mutual Precipitation of Colloids

In close association with the coagulation by electrolytes is the mutual precipitation of two colloids having charges opposite to each other in nature. Many investigators have worked with this phenomenon, but Biltz was the first to give a satisfactory explanation.† Graham remarked this mutual precipitation, while Picton and Linder ‡ made the observation during their investigations with solutions of dyestuffs, that

* A. v. Galecki: Zeit. f. Elektrochemie, **14**, 767–768 (1897).
† W. Biltz: Ber., **37**, 1095–1116 (1904).
‡ H. Picton and S. E. Linder: Journ. Chem. Soc., **71**, 568–573 (1897).

mixtures of those with charges opposite in sign were mutually precipitated. On the other hand those with like charges had no effect on each other. Similar effects were noted by Lottermoser * with colloidal iron oxide, silicic acid, and several other colloids. He endeavored to determine the composition of the precipitate, but the experiments were frustrated by difficulties in washing it, owing to its colloidal nature.

Contrary to the experiences of Picton and Linder, certain observations of Spring † seemed to upset all the rules made up to this time for the mutual precipitation of colloids. It remained for the excellent work of Biltz, however, to elucidate the relations and give us a very important orderly arrangement in this part of colloidal chemistry. According to the law that obtains in these cases, colloids having opposite charges always precipitate each other if they are mixed in the proper proportions. On the contrary if either one is present in an appreciable excess there will be no coagulation. Herein lies the cause of Spring's anomalous results; the mixture was not made in the requisite proportions. About the same time Bechhold,‡ Neisser and Friedmann,§ Victor Henri ¶ and his fellow workers, all obtained results similar to Biltz. Some of Biltz's results are given in Table 11. This

TABLE 11

Sb_2S_3-sol. against Fe_2O_3-sol.
2 cc. of the sulfide solution = 0.56 mgs. Sb_2S_3.
13 cc. iron oxide solution of variable concentration.

mg. Fe_2O_3	Observations made immediately after mixing.
20.8	Turbid, but homogeneous.
12.8	Turbid, but homogeneous.
8.0	Flocculent precipitate slowly settled out. Solution yellow.
6.4	Complete precipitation.
4.8	Formation of flocks, solution yellow.
3.2	Few flocks, solution yellow.
0.8	Turbid, no flocks, solution yellow.

table shows that to obtain a maximum precipitating effect a definite relative concentration must be maintained, and that if this relation is exceeded too far in either direction there will be no coagulation. In

* A. Lottermoser: Anorganische Kolloide, page 76. Stuttgart (1901).
† W. Spring: Bulletin de l'Acad. Roy. de Belg. (3), **38**, 483–520 (1900).
‡ H. Bechhold: Zeit. f. phys. Chemie, **48**, 385–423 (1904).
§ M. Neisser und U. Friedmann: Münch. med. Wochenschr., **51**, 465–469, 827–831 (1903–4).
¶ V. Henri, Lalou, Mayer et Stodel: Comp. rend. des séances de la Soc. de Biol., **55**, 1666 (1904).

this respect mixtures of colloids differ from those of electrolytes. Barium chloride and Glauber salts always give a precipitate regardless of the relative amounts added. The amount of the residue is regulated by the substance present in lesser quantity.

The precipitation of the mixture only within certain fixed limits of concentration is explained by the fact that the electric charges on the particles must be completely neutralized before the maximum coagulation can be obtained. If one or other of the two colloids is present in excess, the oppositely charged particles will unite, and only those unions that are exactly neutral will be precipitated. Finally when one constituent is present in large excess there is no neutralization of the ultramicrons because the substance in the smaller quantity is completely adsorbed by the one present in excess. The aggregates thus formed will have the same charge as the colloid present in the larger amount. Similar relations are met with sometimes when, at great dilution, very insoluble precipitates are formed in solutions of crystalloids. The essential conditions for the formation of a sol by precipitation reactions are that one ion should be adsorbed to a greater degree than the other. See Chapter V on colloidal silver.

Biltz * found further that where acid and basic dyestuffs had opposite charges and were mutually precipitated, the formation of an insoluble chemical combination could be assumed. This corresponds to what is known of acid and basic dyestuffs in the state of crystalloids; namely that they unite, and when the combination is insoluble a precipitate is of course formed. Doubtless such reactions occur in the case of many dyestuffs. The more colloidal the character of these dyestuffs the more nearly will the laws of colloidal reaction obtain. Moreover Biltz has pointed out that with colloids of the nature of gold such chemical reactions are not possible. Nevertheless colloidal gold is precipitated by positively charged dyestuffs. The cause is doubtless the neutralization of the charge on the particles. For further particulars attention is called to Chapter XI.

Absorption and Adsorption

It is very well known that comparatively large quantities of carbon dioxide and ammonia are condensed by porous substances, such as charcoal, meerschaum, etc., although no chemical reaction occurs between them at the temperature in question. In fact charcoal will not only take up gases, but even dyestuffs and salts of the heavy metals can be removed from a solution by this means. Use is made in the industries of this property to clarify sugar, to remove fusel oil from

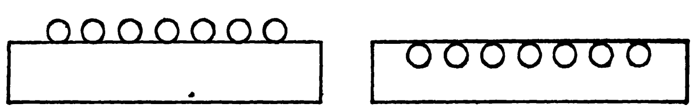
* W. Biltz: Ber., **37**, 1111 (1904).

alcohol and alcoholic beverages, to take bad smelling substances from gas mixtures, and in gas masks in warfare.

The taking up of gases and dissolved substances by charcoal was looked upon as a reaction analogous to the dissolution of a gas by liquid, and was therefore given the name, *absorption.* The characteristics of the phenomenon were that the gas penetrated into the interior of the porous body. Later a distinction was made between absorption and adsorption. The former was employed if the gas penetrated into the body; the latter when the gas was condensed on the surface. (Mueller and Pouillet.*) From this point of view van Bemmelen designated the taking up of gases and dissolved substances by hydrosols as absorption and not adsorption. The nomenclature was justifiable at the time, because there can be no question but that the substance taken up penetrates the entire mass, and does not remain on the outer surface as does gas on pieces of quartz or glass.

Since porous substances and hydrogels have come to be regarded as heterogeneous systems having numerous walls or partitions throughout the mass, the term adsorption has again been used, with the corresponding limitations on the term, absorption. It is open to question, however, whether the taking up of gases and dissolved substances by hydrogels is solely a surface phenomenon. Van Bemmelen and others have argued against this point of view. Details cannot be dealt with here; a fundamental principle, however, will be elucidated.

Imagine two bodies, each homogeneous in itself, touching each other but sharply differentiated at the point of contact, such as a quartz crystal or glass and air. That is to say, there shall be no solution of one in the other. Their common border is a true surface in the geometric sense. It is clear that on such a two-dimensional surface no substance occupying three dimensions can accumulate. When, however, a gas condenses on the surface of a solid body it must either



Pure Adsorption.

FIG. 11. Penetration of gases, etc., through the outer surface.

accumulate in a layer on the outer surface, or penetrate the latter to a certain distance. Both effects are illustrated in Fig. 11. Examples of both these phenomena are known. According to Weidele † the well-

* Müller-Pouillet: Lehrbuch der Physik (9. Aufl.), 1, 589. Braunschweig (1886).

† *Ibid.*

known frost figures on the window pane arise from the gas that has been condensed on the surface. On the other hand, the cracks and bubbles that occur when an old piece of glass is being heated are due to water and carbon dioxide that have penetrated the glass.

Only in the case where the condensation occurs on the outer surface is the term adsorption appropriate. Although water vapor and carbon dioxide reach the interior of many bodies, the penetration of crystals is confined to a very thin layer while the composition of the interior remains unchanged. Quite different will be the conditions when a solid is in thin layers or lamellæ. If the lamellæ are thinner than the distance to which the gas will penetrate, the composition of the entire mass will, of course, change. As a consequence the properties of a substance in the form of lamellæ may be quite different from those of the same body in a more compact state. In the latter case the phenomenon is purely one of adsorption, while the lamellæ either absorb the gas, or a combination of both adsorption and absorption may occur. Colloidal particles of hydrogels may be regarded as extraordinarily fine lamellæ, and although we cannot decide definitely whether the condensation is purely a surface phenomenon or a penetration (probably both), it seems justifiable with van Bemmelen to designate the taking up of gases and dissolved substances by hydrogels as absorption. Doubtless the case is very complicated, for even chemical reactions may occur. From these considerations it would perhaps be better to drop both terms in doubtful cases and employ the expression, sorption, as has been suggested by McBain.* It seems doubtful, however, whether it would be practicable to change the nomenclature of so many authors. Especially is this so because of the fact that good grounds exist for believing that the taking up of dissolved substances by hydrogels is in reality chiefly a matter of surface phenomena.

It is worthy of note that the accumulation of dissolved substances on the surface of other bodies is very general. Gibbs † has shown that it must come to pass whenever the dissolved substance lowers the surface tension. A great many cases are known where there is neither chemical reaction between the adsorbing and the dissolved substances; nor does the latter penetrate the former. Moreover, because hydrogels doubtless contain a large number of inner surfaces or partitions, true adsorption must play an important part. This is also true of hydrosols where the total surface is enormous.

As might be expected the accumulation on the surface takes place

* J. W. McBain: Zeit. f. phys. Chem., 68, 471-497 (1908).

† J. W. Gibbs: Thermodynamische Studien. German translation by W. Ostwald. Leipzig (1892).

much more rapidly than the penetration into the interior. Freundlich * has demonstrated that adsorption equilibria are reached very quickly, while many cases occur where equilibrium is difficult to obtain. He has assumed that the delay is caused either by chemical reactions or by the penetration of the dissolved substance into the interior of the solid.

The term adsorption will be used in this book with the understanding that all the phenomena described under this head are not necessarily surface reactions. The literature on this subject is so vast that none but the most salient points can be taken up here. For comprehensive discussions reference should be made to W. Ostwald,† Wo. Ostwald,‡ and to Freundlich.§

In order to obtain a comprehensive view of the numerous facts involved some classification is necessary. The following one has been adopted for the present purpose.

1. Adsorption of dissolved crystalloidal substances by bodies having smooth surfaces, and by porous or powdered substances.

2. Adsorption of dissolved crystalloidal substances by hydrogels whereby:

(*a*) The adsorbed material accumulates, but the gel remains practically unaltered in its properties.

(*b*) The composition of the gel is changed, and the new substance itself becomes a hydrosol. (Chemical reactions are generally involved.)

3. The adsorption of dissolved crystalloidal substances by the ultramicrons of colloidal solutions. Thereby:

(*a*) The system may remain apparently unchanged.

(*b*) Precipitation (coagulation) of the ultramicrons may occur, following the neutralization of the charges on the particles by ions of opposite sign. Doubtless chemical reactions frequently take place here also.

4. Adsorption of colloidal substances by bodies having distinct surfaces, such as powders, charcoal.

5. Mutual adsorption of ultramicrons. For instance, protective colloidal effects.

Other classifications are possible. Freundlich, for example, considers the accumulation of substances on the surface under the headings: Solid-gas, solid-liquid, liquid-liquid, liquid-gas.

* H. Freundlich: Zeit. f. phys. Chemie, 57, 385–470 (1907).

† W. Ostwald: Lehr. d. allgem. Chemie (1 Aufl.), 1, 778–791 (1885); (2 Aufl.) 2, 3, 217 ff. (1906).

‡ Wo. Ostwald: Grundriss der Kolloidchemie, 390–445. Dresden (1909).

§ H. Freundlich: Kapillarchemie. Leipzig (1909).

1. Adsorption of Dissolved Crystalloidal Substances. — As has already been stated, Gibbs, from theoretical considerations, arrived at the conclusion that substances tending to lower the surface tension of a solution against another phase, must be adsorbed by this solution. Further, small amounts of the dissolved substance may lower the surface tension a great deal, but cannot raise it very much.* These laws have been qualitatively proved in many instances. They obtain for crystalloids as well as for colloids. The investigations must be confined to liquid-gas or liquid-liquid systems, for it is only in these cases that the surface tension can be determined with accuracy. Freundlich has shown that those substances which greatly lower the surface tension of liquid against liquid are not only adsorbed by these, but are also strongly adsorbed by solids. Moreover, he has demonstrated that adsorption isotherms (which give the relations quantitatively) apply to both the surface liquid-gas and liquid-liquid.

W. Ostwald † showed that adsorption is reversible and that the equilibrium could be reached from both sides. A large number of determinations by various investigators have shown that the quantitative adsorption of dissolved crystalloidal substances in relation to the end concentration can be expressed by Freundlich's purely empirical formula

$$\frac{x}{m} = \alpha \cdot c^{\frac{1}{n}},$$

where x is the amount adsorbed, m is the amount of adsorbing substance, c is the end concentration, and α and $\frac{1}{n}$ are constants that depend upon the nature of the substances in question.

Other formulas are in use. The following one of G. C. Schmidt ‡ holds very well for the adsorption of acetic acid by charcoal.

$$\left(\frac{a - x}{v}\right) S = K \cdot e^{\frac{A(S - x)}{S}} \cdot x,$$

where a is the original amount of dissolved substance, x is the amount adsorbed, v is the volume, S is the maximum adsorption, and A and K are constants. Svannte Arrhenius § has recently evolved another equation from theoretical grounds.

$$K\frac{dx}{dc} = \frac{(s - x)}{x}, \text{ or integrated, } \log\frac{s}{s - x} - 0.4343\frac{x}{s} = \frac{1}{k}c.$$

* J. W. Gibbs. Thermodynamische Studien, 321.

† W. Ostwald: Lehrb. d. allg. Chemie, 789 (1 Aufl.).

‡ G. C. Schmidt: Zeit f. phys. Chemie, **77**, 641–660 (1911). R. Marc: Zeit. f. phys. Chemie, **76**, 58–66 (1911).

§ Svante Arrhenius: Meddelanden från. K. Vetenskapsakad. Nobelinstitut, **2**, No. 7 (1911). G. C. Schmidt: Zeit. f. phys. Chemie, **78**, 667–681 (1912).

Here x is the amount of adsorbed substance on 1 gm. of charcoal, s is the maximum value of x, c is the pressure of the gas or the osmotic pressure of the dissolved substance, and k is a constant.

Attention is called to the fact that, according to van Bemmelen,* the isotherms already mentioned, within certain limits, apply to the taking up of crystalloids by charcoal as well as by hydrogels.

The value of $\frac{1}{n}$ according to Freundlich varies from 0.1 to 0.5. The values of α vary within wide limits. For example for the system

Acetic acid in water and charcoal from blood........$\alpha = 2.6$
Bromine in water and charcoal from blood..........$\alpha = 23.1$

For specific information in this field the original work of Freundlich should be consulted. It should not be overlooked, however, that the adsorption isotherms already given are typical for true adsorption phenomena; and wherever these isotherms fit the case many experimenters regard the reactions as pure adsorptions, even when there is some evidence to the contrary. It should also be remembered that the formula has no theoretical foundation, and that the incorporation of two constants makes it a very flexible interpolation formula.

The theoretically grounded formula of Arrhenius containing one constant assumes the adsorption to be due to molecular attraction between the gas or dissolved substance and the adsorbing material. It is in close association with the compressibility of the liquids and is not connected with capillarity.

2. **Adsorption of Dissolved Crystalloidal Substances by the Ultramicrons of Hydrogels.** — The taking up of dissolved crystalloidal substances, during which a spontaneous subdivision of the hydrogel occurs, will be discussed with the theory of peptisation in Chapter IV.

3. **Adsorption of Crystalloidal Substances by the Ultramicrons of Colloidal Solutions.**† — An example of this has already been considered on page 38.

4. **Adsorption of Colloids by Other Substances.** — Cases where a colloid can be completely removed from a liquid by porous bodies, powder, or jelly-like substances, are of common occurrence.‡ Colloidal gold can be separated from the liquid by animal charcoal, barium sulfate, or aluminium hydroxide gels. The process may be followed

* J. M. van Bemmelen: Journ. f. prakt. Chemie (2), **23**, 324–349, 379–395 (1881); Zeit. anorg. Chemie, **23**, 111–125, 321–372 (1903).

† A. Lottermoser und P. Maffia: Ber. **43**, 3613–3618 (1910). Wo. Ostwald: von Bemmelen-Gedenkboek, 246–274 (1910).

‡ R. Zsigmondy: Verh. d. Ges. D. Naturf. u. Ärtze, 73. Vers., 168–172. Hamburg, (1901). L. Vanino: Ber., **35**, 662 (1902). W. Biltz: Nachr. d. Kgl-Ges. d. Wiss. Göttingen, Math. phys. Kl., 46–63 (1905).

partially at least with the ultramicroscope. It is improbable that electric charges play a part here because animal charcoal and colloidal gold are both charged negatively. It is much simpler to assume some specific attraction between the adsorbing substance and the gold.

Many colloids other than gold can be removed from solution by the same method. As a lecture experiment the author uses the adsorption of molybdenum blue by animal charcoal. The dark blue liquid becomes quite colorless on shaking and filtering. As in many other cases the adsorption is quantitative and irreversible.

It is assumed by many investigators that during adsorption only that part of the substance present as crystalloid is taken up. This is probably true in many cases; as, for instance, in coloring with dyestuffs where the portion present as crystalloid is large and the remainder is in the form of relatively large particles. This point of view is untenable, however, in the case of true colloids where the part dissolved as crystalloid is very small. Here it must be assumed that the colloidal particles are themselves adsorbed. In specific instances this can be verified experimentally as in the case of gold and aluminium hydroxide gels.

Mutual Adsorption of Ultramicrons. Protection Effects.—The adsorption of colloids by finely divided charcoal is closely allied to the taking up of colloids by the ultramicrons of other colloids. It plays as important a rôle in the precipitation of colloids as it does in protective effects. In general the protective colloid is taken up or adsorbed by the particles of the irreversible colloid, even though the signs of the electric charges are the same. Occasionally the process is reversed, and the particles of the irreversible are adsorbed by the protective colloid. This last phenomenon may be followed under the ultramicroscope when the protective colloid is present in a not too fine state of division. See Chapter V.

The cause of the protective effect is a union between the particles of different colloids. Ultramicrons of an irreversible colloid, that have taken up a sufficient number of particles of a protective colloid, have lost the property of coagulation either on the addition of an electrolyte, or on evaporation. The protective effect of specific colloids varies greatly. A basis for comparison may be found in the determination of the gold number. This together with other points of interest will be discussed in Chapter V.

Influence of Temperature on Colloids

At higher temperatures colloids are in general less stable than at lower. The specific members, however, differ very greatly in this regard. As an instance of this colloidal gold solutions may be cited. If

made according to the author's procedure the solution will withstand heating at the boiling temperature for a long time without suffering any change. On the contrary Faraday's colloidal gold will coagulate at the boiling point, as will also the platinum hydrosols prepared according to Bredig's method. Graham's colloidal aluminium hydrate solutions could be heated to the boiling temperature with impunity; they coagulated, however, if the boiling were continued. Many irreversible hydrosols exhibit a similar behavior. Schneider * has reported that colloidal silver coagulates completely if the solution is heated in a closed tube to the critical temperature. Protein solutions coagulate considerably under the boiling temperature, while gelatin in solution, on the other hand, becomes more finely divided at the higher temperatures.

Freezing of Colloids. — On freezing the disperse medium, colloids show a great variation in behavior. Many of them suffer irreversible changes so that after the thawing out of the frozen mass, they no longer form a colloidal solution, but are coagulated into jellies, powders, or fine flakes. Pure metal hydrosols are completely precipitated and the residue cannot be returned to the colloidal state. Protected metal colloids, on the contrary, may be frozen repeatedly without coagulation occurring. In the case of colloidal sulfides and oxides the amount of peptising agent present is of importance. In general it may be said, the more stable a colloid is toward electrolytes and evaporation, the more stable it will be to freezing. In this connection Ljubavin† found that colloidal iron oxide suffered a change on freezing only if it had been previously well dialyzed. Lottermoser ‡ corroborated this result and showed that the colloid would coagulate on freezing if it were nearly free from electrolytes. It was also noticed that the conductivity of the system was increased by the freezing. This can be accounted for on the grounds that the particles give up the adsorbed ions, which are necessary for the stability of the colloid, and suffer an irreversible change. On melting the mass the colloid has thus lost the property of peptising. Gelatin, sturgeon bladder, carrageen, agar-agar, and sapo medicatus change so that the first portions of the liquid after melting the frozen mass contain scarcely any of the dissolved substance. After complete thawing out the mass is inhomogeneous, consisting of thin liquid and flocculent jelly. At room temperature the process of redissolution is not complete after 48 hours.§

* E. A. Schneider: Zeit. f. anorg. Chemie, **3**, 78–79 (1893).

† K. Ljubavin: Journ. russ. phys. chem. Ges., 21, **1**, 397–407 (1889). Ref. Koll.-Zeit., **1**, 53 (1906).

‡ A. Lottermoser: Zeit. f. phys. Chemie, **60**, 462 (1907); Ber., **41**, 3976–3979 (1908).

§ O. Bobertag, K. Feist und H. W. Fischer: Ber., **41**, 3675–3679 (1908).

During his work on the effect of low temperatures on plants, Molisch * investigated the changes in jellies brought about by freezing. Fig. 12 shows how the gelatin arranges itself in a network of cellular structure around the tiny lumps of ice. H. Ambronn † has shown that the colloidal net of gelatin or agar-agar resembles in many respects a parenchymous plant tissue. In optical properties the walls of the net are very similar to the cell walls of a normal plant. Ambronn also demonstrated that ice flowers may be fixed upon a glass plate if a solution of gum is spread out upon it, allowed to freeze, and the ice evaporated at low temperatures. An interesting physico-chemical phenomenon was discovered by H. W. Fischer,‡ who studied the rate of cooling of different jellies. He found that the curve below the freezing point did not always correspond with that of water.§ From this it was concluded that jellies undergo changes on freezing by which heat is evolved.

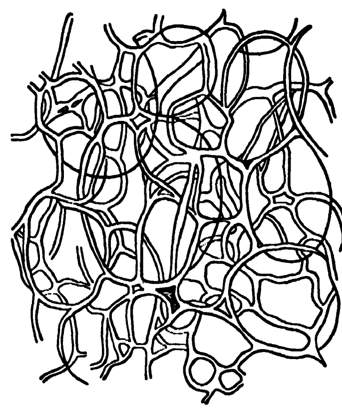


Fig. 12.

Similar changes of state take place on freezing in the case of plants and animal tissues. The analogy to the behavior of hydrogels is quite striking. Both in the case of jellies and in that of leaves, fruit, and muscles after thawing the mass, the water is not so firmly held as before the freezing. Mere freezing does not necessarily destroy the hydrosols. The temperature of the gelatin solution must be lowered to such a degree that irreversible changes come to pass. For the state of the water in the muscles after freezing, see the article by P. Jensen and H. W. Fischer.¶

Heat of Colloidal Reactions

The heat of colloidal reactions is generally very small. That it is appreciable during distension and dissolution of gelatin has been shown by Wiedemann and Luedeking.|| The results for irreversible colloids

* H. Molisch: Untersuchungen über das Erfieren der Pflanzen. Jena (1897).

† H. Ambronn: Verh. d. Kgl. sächs. Ges. d. Wiss. Leipzig Math. phys. Kl., **43,** 28–31 (1891).

‡ H. W. Fischer: Beitrage zur Biologie der Pflanzen, **10,** 133–234 (1910).

§ H. W. Foote and Blair Saxton, Jour. Am. Chem. Soc., **38,** 588 (1916).

¶ P. Jensen und H. W. Fischer: Zeit. f. allg. Physiol, **11,** 23–93 (1910).

|| E. Wiedemann und Ch. Lüdeking: Wiedemanns Annalen (N. F.), **25,** 145–153 (1885).

are often contradictory. For instance, J. Thomsen * observed no heat of reaction during the coagulation of silicic acid, while Wiedemann and Luedeking obtained 11.3 to 12.2 calories per gram. Graham † observed a rise in temperature of one degree during the coagulation of a 5 per cent gèlatin solution. According to Picton and Linder ‡ there is no measurable heat of reaction during the gelatinizing of As_2S_5, As_2S_3, and Fe_2O_3.

A very careful research by Doerinckel § has demonstrated that the heat of reaction during the coagulation of silicic acid and also of iron oxide is always positive. Its relation to the concentration of the hydrosol and to that of the precipitating agent is shown by the curves in Figs. 13 and 14. The ordinates give the heat of reaction in calories

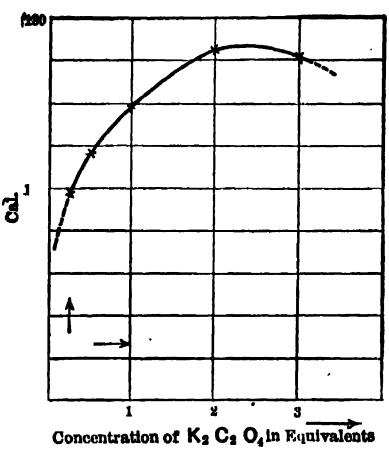


FIG. 13. Heat of coagulation of a 10.8% solution of Fe_2O_3 by $K_2C_2O_4$.

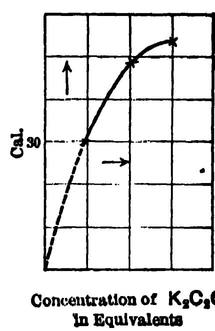


FIG. 14. Heat of coagulation of a 5% solution of Fe_2O_3 by $K_2C_2O_4$.

for 250 cc. of the solution, while the abscissas give the concentration of the precipitating reagent in equivalents per liter. The heat of coagulation as a function of the amount of the adsorbed electrolyte is shown in Fig. 15. The heat of coagulation depends among other things upon the nature of the precipitating agent. The value obtained by Doerinckel for the precipitation of iron oxide by potassium oxalate is almost three times as great as that by aluminium sulfate. The investigation proved further that the heat evolved is not a linear function of the concentration of the colloid. The linear extrapolation generally gives

* J. Thomsen: Thermochemische Untersuchungen, 1, 211–219. Leipzig (1882).

† Th. Graham: Poggendorffs Annalen, **123**, 529–541 (1864).

‡ H. Picton and S. E. Linder: Jour. Chem. Soc., **61**, 144, 146–153 (1892).

§ F. Doerinckel: Zeit. f. anorg. Chemie, **66**, 20–36 (1910).

a value greater than zero. From this it will be seen that the heat of coagulation is greater per gram iron oxide for dilute solutions than it is for the more concentrated. The cause of this deviation is doubtless the fact that when the more concentrated solutions are mixed, membranes of the precipitate are formed. These membranes prevent a thorough mixture of the two solutions, and there is not a complete precipitation of the iron oxide during the time of the observation.

The heat of coagulation is also dependent upon the amount of peptising electrolyte present.

Very interesting also is the experimental result obtained by Doerinckel * in regard to the relation of the concentration of the two components in the mutual precipitation of colloidal silver (Argoferment,

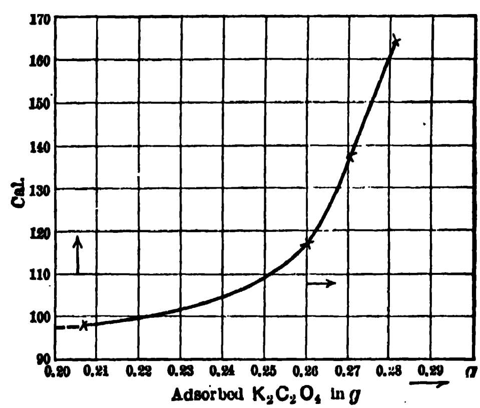


FIG. 15. Heat of coagulation of 250 cc. Fe_2O_3 solution as function of adsorbed $K_2C_2O_4$.

Heyden, Radebeul) and colloidal iron oxide. As much as 47 cals. for every 2.5 gms. of the disperse phase were evolved. The maximum heat of reaction and the precipitation did not correspond. The argoferment contained an appreciable amount of protective colloid that did not take part in the reaction. In the case of the reversible precipitation of argoferment with ammonium nitrate a very small heat of reaction was observed, namely between 1 and 2 cals. for every gram of silver. Prange,† on the other hand, working with pure colloidal silver found 126.7 and 250.9 cals. for 1 gm. silver. From this it would appear that the preparation of the sample plays an important part, after allowance is made for the inaccuracy of Prange's results. These results explain the contradictory observations of different investigators. Different

* F. Doerinckel: Zeit. f. anorg. Chemie, 67, 161–166 (1910).

† J. A. Prange: Recueil d. travaux chim. des Pays-Bas, 9, 121–133 (1890).

heats of coagulation may be obtained according to the method of preparing the colloidal solution, the amount of electrolyte present, the fineness of the subdivision, and the nature and the concentration of the precipitating reagent. Attention should be called to the apparatus employed by Prange during these measurements for which reference must be made to the original article.

Constitution of Jellies

Jellies may be obtained from colloidal solutions as well as from colloidal solids by a large number of methods. They may also differ markedly in their properties and their structure. In fact it is difficult to make general statements about the matter. On the one hand the hydrogel of silicic acid is obtained by the coagulation of the hydrosol, and neither by dilution with water nor by warming can the colloidal solution be reformed. On dehydration a glassy porous solid is left, which will be discussed in a later chapter. On the other hand gelatin jellies are made by the distension of solid gelatin in water, or by cooling the solution which was obtained by the aid of heat. The gel becomes a liquid on warming and returns again on cooling. On evaporation a transparent solid remains that will again distend in water and become a hydrosol. Agar-agar and starch behave similarly. Coagulated albumin is an opaque cloudy gel that shrivels to a transparent mass. This mass will distend in water to form a hydrosol.

Concerning the structure of gels a great many investigators have occupied themselves without coming to any very definite understanding. Biologists as well as chemists and physicists have been engaged in this work. The oldest theory assumed a porous structure for distensible bodies. The water penetrated into the pores and caused them to swell. The water, therefore, was considered as being held by capillary or by molecular attraction. In 1858 Nägeli * called attention to the very great difference between porous bodies, on the one hand, and gels on the other. He proposed a theory that with some modifications explains, according to the view of the author, the structure of gels. Nägeli pictured distensible bodies as small anistropic, crystal-like molecular complexes or tiny crystals, that cause the double refraction because of their orientation. According to this theory the distension is occasioned by the penetration of water into the micellular walls in such a manner that the micells are surrounded by a layer of water. The thickness of the sheath is regulated by the fact that the attraction of the micells for the water molecules diminishes faster with the distance than does

* C. v. Nägeli und S. Schwendener: Das Mikroskop (2. Aufl.). Leipzig (1877). C. v. Nägeli: Theorie der Gärung, 121 ff. München (1879).

the attraction of the micells for one another.* When dissolution of the colloid takes place it does not divide up into individual molecules, but rather into these molecular complexes or micells. As a matter of fact we know that the presence of ultramicrons is one of the most common occurrences, and in some cases a lamellar, anisodiametrical formation of these ultramicrons has been observed. We also know that the particles contained in hydrosols are not the molecules of the substance in question, but are larger complexes.

Bütschli † carried out some very thorough experimental investigations on the structure of distended substances. He found that many jellies possessed a fine honeycomb micro-structure, and sought for evidence to show that jellies homogeneous to the microscope were also of a honeycomb formation. In order to render the structure visible Bütschli employed many devices, such as the hardening of gelatin gels by alcohol or chromic acid. By this treatment the jellies become turbid and more suitable for microscopical investigation. He began with a research on the structure of foams, obtained by the distension of oils containing soap in water.‡ In such a system a honeycomb structure is formed, the walls of which are oil lamellæ while the enclosed spaces are filled with water. Similarly distended jellies are heterogeneous. The small cells are filled with water while the extremely thin walls are composed either of the distended substance, a combination of it with the water, or a solid solution of water in the substance. The walls Bütschli considers permeable to liquids because of their extreme thinness. Thus a diffusion reaction may occur between the enclosed water and another liquid, such as alcohol. He admits, however, that the walls may also be porous but that these pores cannot be seen by the microscope and must therefore be very small.

Wolgang Pauli § has raised an objection to the assumption that the structure of gels was not altered by the hardening process with alcohol, or with chromic acid. His view has been substantiated somewhat by experimental results obtained in the laboratory of the author. The ultramicroscopy of gelatin gels, as well as of semi-liquid hydrosols of silicic acid, has shown that the structure of gels is granular or flocculent rather than honeycombed. The observation of the formation of a

* Nägeli: Theorie der Gärung, 148.

† O. Bütschli: Über den Bau quellbarer Körper usw. Göttingen (1896). Untersuchungen über Strukturen. Leipzig (1898). Untersuchungen über die Mikrostruktur künstlicher und natürlicher Kieselsäuregallerten. Heidelberg (1900) u. a.

‡ O. Bütschli: Untersuchungen über mikroskopische Schäume und das Protoplasma. Leipzig (1892).

§ W. Pauli: Der kolloidale Zustand und die Vorgänge in der lebendigen Substanz. Braunschweig (1902).

gel from submicrons in motion also substantiates this view. See Chapter XII.

Careful investigation of the hydrogel of dried silicic acid has shown that the structure is much finer than Bütschli assumed. As a matter of fact we are dealing with an almost homogeneous mixture of air and silicic acid; that is to say, a conglomerate of silicic acid amicrons permeated with amicroscopic empty spaces.

The results that have been obtained up to the present time with the ultramicroscope are far more favorable to Nägeli's theory of distensible bodies, than to that of Bütschli. As already pointed out the phenomena of distention is not so simple as Nägeli assumed in that a larger heterogeneity, discovered by Bütschli, is often superimposed upon a finer discontinuity.

Weimarn * has pointed out that gels may be formed simultaneously with crystalline precipitates from solutions of high concentration, where only crystals will be obtained if the concentration is not so great.

* P. P. von Weimarn: Zur Lehre von den Zustanden der Materie Koll.-Zeit., 2–5 (1907–1909).

CHAPTER IV

THEORY

The discussion that follows is not by any means a summary of the theories that have appeared on colloidal chemistry up to present time. Such a comprehensive presentation would be entirely beyond the scope of this book.* On the contrary the author, with due consideration of the work of other investigators, has endeavored to present a point of view that has been prompted by years of personal observation and thought, and which at the same time gives a simple and comprehensive explanation of the largest number of facts. For purposes of illustration constitution formulas have been made use of, such as the author has previously employed in his monograph, "Zur Erkenntnis der Kolloide."

The hypothesis, that the electric charge on irreversible hydrosols is due to the adsorption of ions on, or the giving up of ions by, the particles, seems capable of explaining an enormous number of experimental facts. The principles of this point of view, arising out of Hardy's work, were first presented by Bredig, and more fundamentally dealt with by Billitzer. The author had independently employed the same hypothesis to explain peptisation and the reactions of the purple of Cassius. These considerations were not published until 1904.

Cotton and Mouton favored the electric double layer theory of Helmholtz. Duclaux, who with Jordis had considered hydrosols of

* Arth. Müller: Die Theorie der Kolloide. Leipzig u. Wien (1903). Allgemeine Chemie der Kolloide. Leipzig (1907). Wo. Ostwald: Grundriss der Kolloidchemie. Dresden (1909). H. Freundlich: Kapillarchemie. Leipzig (1909). W. B. Hardy: Zeit. f. phys. Chemie, **33**, 326–343, 385–400 (1900). G. Bredig: Anorganische Fermente. Leipzig (1901). F. G. Donnan: Zeit. f. phys. Chemie, **37**, 735–743 (1901); **46**, 197–212 (1903). J. Billitzer: Zeit. f. phys. Chemie, **45**, 307–330 (1903); **51**, 129–166 (1905). E. Jordis: Neue Gesichtspunkte zur Theorie der Kolloide. Berichte d. phys.-med. Sozietät Erlangen, **36**, 43–107 (1904). Koll.-Zeit., **2**, 1–7; **3**, 1–27 (1908). R. Zsigmondy: Zur Erkenntnis der Kolloide. Jena (1905). A. Cotton et H. Mouton: Les ultramicroscopes et les objects ultramicroscopiques. Paris (1906). L. Michaelis: Physikalische Chemie der Kolloide. Leipzig (1908). P. P. von Weimarn: Zur Lehre von den Zuständen der Materie. I. Teil. Dresden (1908). II. Teil in Koll.-Zeit., **3** u. **5** (1908 u. 1909). J. Duclaux: Journ. de Chim. Phys., **7**, 405–463 (1909). G. Malfitano: Kolloidchem. Beihefte, **2**, 142–212 (1910). A. Lottermoser: Zeit. f. phys. Chemie, **60**, 451–463 (1907); **62**, 359–383 (1908); **70**, 239–248 (1910). Koll. Zeit., **6**, 78–83 (1910).

the type of iron oxide as solutions of complex ions, later accepted the theory that electrolytically charged particles were present. Duclaux has dedicated some very careful work to the theory of the osmotic pressure and the conductivity of irreversible sols. Further, the adsorption of ions has been assumed by Freundlich and Lottermoser, while the dissociation of molecules on the surface of the particles has been advocated by L. Michaelis.

Because of the lack of space the theory of the electric double layer will not be taken up in detail. Neither will there be any lengthy discussion of the question raised by Freundlich as to whether the adsorbed ions are on the surface of the particles, or in the water layer immediately surrounding the particles. From the results obtained by Freundlich the last supposition seems a very probable one, but there is no necessity for discussing the problem here.

All the fundamental methods employed in colloidal chemistry, the Tyndall effect, ultramicroscopy, ultrafiltration, and finally the application of osmotic pressure point unmistakably to the conclusion that the particles, although they are at times very small, are nevertheless much larger formations than the molecules of crystalloids.

The first question that presents itself is the cause of the stability of colloidal solutions. It is advisable to consider the two great classes separately; the reversible, those that subdivide spontaneously; and the irreversible, those that lack the property of spontaneous subdivision.

1. *Reversible Colloids.* — The causes for the stability, and also the solubility, of hydrosols of the reversible colloids is not clearly understood. The solubility probably is occasioned by the same influences that govern the solubility of crystalloids. Reversible colloids may possess a solution tension and the subdivision would therefore occur because of diffusion. Although this may play a part, it is not by any means the only factor at the root of the spontaneous subdivision, because many reversible colloids subdividing very easily in a medium, diffuse with difficulty and exhibit a smaller osmotic pressure than many irreversible. The behavior of Paal's colloidal gold, Lea's silver and Kollargol may be cited as examples. A negative surface tension between the colloid and the water may also be assumed and the dissolution laid to this cause.* A very important and illuminating piece of experimental work pointing toward this view under the assumption of Laplace's theory of capillarity has been performed by Donnan.† Moreover, the adsorption of water is doubtless at the bottom of the disten-

* E. Riecke: Lehrbuch der Physik, 1,289 (3. Aufl.). van der Mensbrugghe: Congrès international de Physique, T. I., 487 (1900).

† F. G. Donnan: Zeit. f. phys. Chemie, 46, 197–212 (1903).

tion of reversible colloids. Perhaps a chemical combination between the ultramicrons and the water also plays an essential rôle. Many of these colloids have the property of causing irreversible colloids to become reversible.

2. *Irreversible Colloids.* — These bodies do not have the property of going into solution spontaneously. The conditions governing the stability of their hydrosols are given in the chapters on metal hydrosols. The most interesting point for consideration here is the charge on the particles, which is fundamental for the stability of the hydrosol. If the particles become discharged the hydrosol coagulates and the precipitate is always isoelectric with the medium. This has been doubted by Billitzer who held that the minimum stability and the isoelectric point did not necessarily fall together. Later experiments by Burton, Svedberg, and von Galecki have confirmed the earlier results of Hardy. Neutral particles may be charged positively with acid, and negatively with alkalis. On this fundamental proposition of Hardy's may be based the most useful theories of coagulation and peptisation.

The causes for the electric charges on the particles have already been discussed in Chapter III. We will merely call attention here to the following possibilities which are of first importance for this part of the discussion.

The Taking up and the Giving off of Ions.— It is the concensus of opinion among a large number of investigators that the adsorption of ions plays an essential rôle in the charge of colloids. Since the publication of the fundamental work of Hardy, the author has been much occupied with this question, and has come to the conclusion that the adsorption and dissociation of ions by the particles offer the only rational explanation of the coagulation and peptisation by electrolytes.

Formation of Chemical Compounds. — Certain experimenters hold that the hydrosols of silicic acid, stannic acid, etc., do not contain these substances as such, but are chemical combinations in solution. According to this point of view colloidal silicic acid is either a solution of alkali silicate having a high molecular weight and a large excess of silicic acid, or a combination of hydrochloric and silicic acid. Similarly stannic acid is a stannate of high molecular weight. Against this viewpoint many objections may be raised.

1. In the first place one would have to assume that chemical compounds may have an almost continually increasing molecular weight. This would entail, according to amount of sodium or chloride present, the inclusion in the category of chemical compounds of a large number of badly defined bodies, and load chemistry with much useless ballast. It would be necessary to assume the presence of compounds having

unusually high molecular weights; for instance one molecular weight of sodium to 500 or 1000 molecular weights of silicic acid. See Chapter VII on the hydrosols of silicic acid.

2. There would be almost no upper limit to molecular weights if the submicroscopical particles were regarded as ions of salts.

3. The hypothesis is not sufficient to explain the alkali solubility of the purple of Cassius, and similar colloidal complexes.

Although this point of view does not sufficiently explain the reactions of irreversible colloids, it must be admitted that there is a strong resemblance between some of these solutions and those of complex salts. The change from colloidal oxides to true electrolytes is so gradual that no sharp line can be drawn between them. It is quite possible that some of these solutions contain electrolytes of high molecular weight, and they do not diffuse through membranes because of the size of the molecules and ions. Such could be true in the case of reversible oxides containing a great deal of peptising agent, and also in the case of some colloidal dye stuffs.

In the following paragraphs a few specific examples will be given to show how peptisation and a number of other colloidal reactions may be explained in a simple manner on the basis of adsorption of ions.

Theory of Peptisation

The theory of peptisation must be preceded by a brief consideration of the history of the ultramicrons during the formation of a gel. Characteristic ultramicrons can be observed in a hydrosol, in the precipitated hydrogel, and once more in the hydrosol after peptisation. The logical conclusion to draw from this fact is that the particles too small to be seen by the ultramicroscope behave similarly. In other words the particles in a hydrogel are identical with those in the hydrosol with the exception that they are much closer together in the former. This is confirmed in the case of the gel of silicic acid where the structure is much finer than was assumed from the experiments of Bütschli. See Chapter VII, on the gel of silicic acid; also the chapter on the change of color of colloidal gold; peptisation of the purple of Cassius. The fact that hydrogels are so easily turned into hydrosols is additional evidence that the particles do not unite to form larger complexes when the gel is formed from the hydrosol.

We must picture to ourselves a gel as consisting of a closely compact mass of ultramicrons of the same kind holding each other together by cohesion. The interstices of a newly prepared gel are, of course, filled with water. It is only necessary to add an electrolyte, one ion of which is more adsorbed than the other, in order to recharge the particles, and

therefore cause peptisation. Let us choose stannic acid on which to further illustrate the action.

If alkali is added to a gel of stannic acid without doubt a small portion of each unite to form a stannate. It is equally certain that a part of the stannate will be adsorbed by the stannic acid. If now the mixture is diluted with water the dissociation of the stannate occurs, and one has but to assume that the stannate ion is more adsorbed by the ultramicrons than the potassium ion in order to explain the peptisation. The stannate ion imparts the negative charge to the particles and the subdivision goes on in a manner very similar to that of diffusion. The potassium ion diffuses to portions of the liquid where the concentration is not so great taking in its wake the stannate ion with its attendant ultramicrons, just as in the case of hydrochloric acid the hydrogen ion leads the way to places of lower concentration and the chloride ion follows.* The reaction may be expressed by means of the following equation:

$$\boxed{SnO_2} + SnO_3K_2 = \boxed{SnO_2}\ SnO_3K_2$$

where $\boxed{SnO_2}$ represents an ultramicron regardless of the real size, form, or composition. The reaction of dilution may be represented thus:

$$\boxed{SnO_2}\ SnO_3K_2 \rightleftarrows \boxed{SnO_2}\ SnO_3^{=} + 2\,K^+ \qquad \text{(B)}$$

The complex $\boxed{SnO_2}\ SnO_3^{=}$ has the properties of a complex ion having two or more valences, and differs from it only in regard to size. It may or may not be hydrated.

Under certain circumstances a very small amount of alkali is sufficient to cause complete peptisation without any further dilution. The direct adsorption of the stannate ion may be assumed. In this case the following reactions come to pass.

1. Diffusion of the KOH into the interior of the clots and the subsequent formation of K_2SnO_3, the anion of which is strongly adsorbed. As a consequence of this reaction the concentration of the K^+ is increased in the interior of the clots.

2. When the concentration of the K^+ is sufficiently great, and the particles correspondingly charged, the attraction between the particles is lessened owing to increased osmotic pressure in the interior of the clots. See page 82 on the theory of membrane equilibria.

3. Diffusion of the charged ultramicrons and the potassium ion molecules into the surrounding liquid.

Instead of the formation of the free stannate and the subsequent adsorption of the anion, one can just as well assume that the stannate

* W. Nernst: Theoretische Chemie, page 367, 5. Aufl.

is formed on the surface of the ultramicrons, and that dissociation takes place here leaving the anion on the particles. It may also be assumed that the ionization on the surface of the ultramicrons takes place thus:

$$|SnO_3H_2 + 2\,OH^- + 2\,K^+ \rightleftarrows |SnO_3^{=} + 2\,K^+ + 2\,H_2O.$$

$|SnO_3H_2$ represents a stannic acid molecule on the surface of an ultramicron. As there is no means of deciding between these assumptions and they all lead to the same result, *viz*: the charging of the ultramicrons and the subdivision of the material, it seems easier to abide by assumption one; that is the adsorption of the ions by the colloidal particles. The fact that this assumption is the more general, and that it may be employed in explaining the formation of mixed colloids, is a further reason for making it. See Chapter VII on Peptoids.

If now an amount of alkali insufficient to cause peptisation is added most of it is taken up by the stannic acid, without entailing any apparent outward change. On adding somewhat more alkali a cloudy liquid is formed, the ultramicrons of which are composed of a number of amicrons. When an excess of the alkali is now added the amicrons may suffer a further subdivision, and finally be completely transformed into stannate. This process has nothing whatever to do with true peptisation.

The subdivision of the ultramicrons, the "Anätzen" of a hydrogel, should by no means be regarded as it has been by many authors. This follows from a consideration of the small amount of alkali necessary to cause peptisation. As shown by experiment the alkali causes a very small diminution in the linear dimensions of the ultramicrons provided that all of them are attacked simultaneously. According to the "Ätztheorie" it is not at all clear why such an insignificant subdivision should cause such a radical change in the properties. This latter theory also does not take any account of the charges on the particles.

If the theory we have adopted is correct, the colloidal solution must exhibit osmotic pressure against a membrane impermeable to the amicrons of the stannic oxide complex; it must possess conductivity and precipitate SnO_2 at the anode during electrolysis, and toward electrolytes must behave similarly to a complex salt of high molecular weight. That all this is true in reality will be shown in what follows.

Nature of the Adsorbed Ions.—The electric charge is equally well explained by the assumption that any anion other than the stannate ion is adsorbed. In the case under consideration the hydroxide ion might be taken up. In view of the following reactions it seems more desirable to assume the adsorption of the stannate ion.

1. The addition of an excess of potassium hydroxide causes the precipitation of the colloidal stannic acid. The ultramicrons are discharged and potassium ion is taken up. Therefore reaction (*B*), page 75, is written reversibly.

2. The discharged ultramicrons are precipitated with the adsorbed stannate. A similar reaction occurs when potassium chloride or any other potassium salt is added.

3. If the hypothesis is correct the precipitated stannic acid must go back into solution when the precipitating agent is removed, because of the renewed dissociation of the adsorbed stannate. This is indeed the case.

4. An extremely small amount of any highly dissociated acid, such as HCl or HNO_3 serves to coagulate the hydrosol of stannic acid.

$$[SnO_2]\, SnO_3^{=} + 2\,H^+ = |SnO_2|\, SnO_3H_2.$$

According to the equation just given stannic acid is formed, which is very insoluble and has very little tendency toward dissociation. The gel should therefore remain as such and not subdivide on the removal of the precipitating reagent. This has been found to be the case.

5. The addition of the salts of heavy metals, such as silver nitrate, causes irreversible precipitation. The precipitate contains a small amount of the cation that cannot be washed out. The precipitate is practically insoluble in pure water because the stannate is itself an insoluble salt.

$$\boxed{SnO_2}\, SnO_3^{=} + 2\,Ag^+ \rightarrow\downarrow \boxed{SnO_2}\, SnO_3Ag_2.$$

Doubtless the real reactions are much more complicated than is indicated by the equation, nevertheless it serves very well to indicate the trend of events in a wide field that is not very easily comprehended.

Consideration of the Behavior of Hydrosols

A. *Ultrafiltration.* — By the use of filters that allow electrolytes to pass freely through, but retain the colloidal particles, colloidal stannic acid must have, after filtration, not only its ultramicrons, with their attendant anions, but also an equivalent amount of alkali ion molecules. The excess of the electrolytes, KOH, K_2SnO_3, etc., that were dissolved in the disperse medium, have passed through. The adsorbed portion of the alkali, regardless of whether it is dissociated or not, is an essential part of the hydrosol; for if it is removed the colloid will coagulate. Duclaux, who has studied the behavior of colloidal iron oxide and cupric ferrocyanide in this connection, has proposed the name "Micells" for the ultramicrons together with their adsorbed molecules

and dissociation products; while the surrounding medium he calls the intermicellular liquid.

B. With reference to the conductivity of colloidal solutions and the filtrates from such, the following may be said:

1. If the ion concentration of the intermicellular liquid is large compared to that of the micells, the conductivity of the filtrate will not differ very much from that which it was before the ultrafiltration. That is, the conductivity of the filtrate and the residue has the same value. Such cases have been observed by Malfitano. See Chapter VII on colloidal iron oxide.

2. On the other hand, if the ion concentration of the intermicellular liquid is relatively small, the conductivity of the filtrate will be lower than that of the residue. Also the conductivity of the residue will increase with increasing concentration, because both the ultramicrons and the attendant oppositely charged ions take part in the transportation of electricity. Duclaux observed an increase in conductivity in the residue after it had been filtered from the liquid.

C. Osmotic Pressure. — The residue must exert osmotic pressure against the filtrate. According to the explanation on page 75, with suitable membranes not only the dissolved molecules, but also the colloidal particles (even suspended particles to a certain degree), must exhibit osmotic pressure. That is to say every particle reacts as a molecule does, the difference being merely one of degree.

In the case we have been studying not only must the complex $\boxed{SnO_2}$ $SnO_3^{=}$ exert osmotic pressure, but also the potassium ion that was adsorbed during the process of the neutralization of the ultramicrons. The total pressure would therefore correspond to the number of particles in the unit volume were it not for the fact that the intermicellular liquid in its partition between the filtrate and the residue causes complications. See Chapter VII. In general this influence is small when the concentration of the intermicellular electrolyte is low compared to that of the colloid.

Duclaux has further observed that the osmotic pressure of colloidal iron oxide after ultrafiltration increases faster than is proportional to the concentration. He explains this on the assumption that the ions dissociated from the particles form an electric double layer around the ultramicrons and that the whole functions as an individual particle. Not until the concentration becomes sufficiently great for the spheres of influence of the individual ultramicrons to cut and cross, can the ions of the micells take part in osmotic pressure.

D. The Effect of Electrolysis. — During electrolysis the complex $\boxed{SnO_2}$ $SnO_3^{=}$ goes to the anode, is there discharged and precipitated.

The cathion migrates toward the cathode where hydrogen is discharged and set free. An interesting reaction comes to pass when a piece of parchment membrane is inserted between the electrodes in the solution. The ultramicrons cannot pass through but are discharged on the membrane and form a gel. To explain this it may be assumed either that the adsorbed anion is set free at the membrane, passes through and continues on toward the anode; or that the discharge takes place because ions of opposite charge meet at the membrane. A closer study of this phenomenon is desirable.

E. Equivalence. — The equivalence referred to in Chapter III between the different amounts of ions necessary to cause precipitation is easily explained. The adsorbed cathions serve merely to neutralize the charges on the anion, and the two must therefore be equivalent when the same amount of the hydrosol is taken. For the sake of vividness the reaction on a single particle may be represented by the reactions:

$$\boxed{SnO_3}\ SnO_3^{=} + 2\,Ag^{+} \rightleftarrows \boxed{SnO_2}\ SnO_3Ag_2$$

$$\boxed{SnO_2}\ SnO_3^{=} + Cu^{++} \rightleftarrows \boxed{SnO_2}\ SnO_3Cu$$

The quantities of Cu^{++} and Ag^{+} necessary to neutralize the charge on a given ultramicron are equivalent to each other. In a manner quite as simple the equivalence between the ions, that may be substituted for each other in the precipitate, may be explained.

Peptisation of Stannic Acid by Hydrochloric Acid

Not only may the peptisation of stannic acid by alkali be explained on the above assumption, but also the peptisation by means of hydrochloric acid is accounted for on the same grounds. It is well known that metastannic acid is insoluble in concentrated hydrochloric acid, and that on dilution it will dissolve to form a cloudy liquid, which has colloidal properties. The reaction is often met with in analytical chemistry. The concentrated acid doubtless forms a stannic chloride and an oxychloride. If we assume that the latter is $SnOCl_2$ and is adsorbed to a considerable degree by the metastannic acid, the peptisation on dilution is explained by the fact that $SnOCl_2$ dissociates, leaving the cathion, probably SnO^{++}, on the colloidal particles of stannic acid, thus causing them to be positively charged. The reaction may be represented thus:

$$SnO_2 + 2\,HCl \rightleftarrows SnOCl_2 + H_2O$$

$$\boxed{SnO_2} + SnOCl_2 \rightleftarrows \boxed{SnO_2}\ SnOCl_2$$

$$\boxed{SnO_2}\ SnOCl_2 \rightleftarrows \boxed{SnO_2}\ SnO^{++} + 2\,Cl^{=}.$$

Peptisation of Other Colloids

The peptisation of most oxides, sulfides and salts may be explained on the same basis. According to Graham the peptisation of ferric hydroxide hydrogel takes place on treating it with ferric chloride. One may assume that the ferric ion attaches itself to the ultramicrons of the colloidal ferric hydroxide, thus imparting to the latter the positive charge.

$$\boxed{Fe_2O_3} + Fe^{+++} \rightarrow \boxed{Fe_2O_3}\, Fe^{+++}.$$

Or one can also assume that an oxychloride is formed and that the cathion is adsorbed by the ultramicrons of the gel, as represented by the following equation.

$$\boxed{Fe_2O_3} + Fe_2O_2^{++} \rightarrow \boxed{Fe_2O_3}\, Fe_2O_2^{++}$$

All the essential qualities of the colloid are accounted for by either of these assumptions.

Arsenious sulfide, like many other sulfides, is peptised by hydrogen sulfide. It is probable that the hydrogen sulfide ion, SH^-, is responsible for the negative charge.

$$As_2S_3 + SH^- \rightarrow \boxed{As_2S_3}\, SH^-.$$

In the case of arsenious sulfide sulfoarsenious acid may be formed and the anion adsorbed by the particles. At present it is difficult to determine which of these points of view is the correct one. In any event the negative charge is occasioned by adsorption of ions, or by ionization on the surface of the particles. The colloidal chemistry of the future will undoubtedly have to deal with the adsorption of ions by ultramicrons.

Colloidal Salts. — In a great many other cases also the use of structural formulas serves to elucidate the processes and the reactions. In the chapters on colloidal salts other instances will be given. Here a single illustration will be taken up, *viz*: the peptisation of cupric ferrocyanide gel by potassium ferrocyanide.

$$\boxed{FeCy_6Cu_2} + FeCy_6^{=} + 4\,K^+ \rightarrow \boxed{FeCy_6Cu_2}\, FeCy^{=} + 4\,K^+$$

The cupric ferrocyanide colloidal particles adsorb the ferrocyanide ion, become negatively charged as a result and go into solution.

Peptisation of Colloidal Combinations

Not only can the peptisation of simple colloidal oxides, sulfides, etc., be explained by the above theory, but also that of colloidal mixtures or "Kolloidverbindungen." The purple of Cassius has been chosen as a representative of this class. Here the purely chemical theory,

that regards the irreversible hydrosols as solutions of salt-like substances having an amphoteric character, fails to satisfy. The purple of Cassius is composed of colloidal gold and colloidal stannic acid, and these two components remain together throughout all the reactions unless the purple of Cassius is actually destroyed. See Chapter V, on the purple of Cassius. Let the formula, $\boxed{Au | SnO_2}$ represent a particle of this substance. There is, of course, no justification for assuming that the complex particle contains only one of each of the components. Furthermore nothing whatsoever is postulated with regard to size, amount, shape, or position in space. The addition of alkali causes the peptisation as a result of the negative charge in precisely the same manner as in the case of stannic acid.

$$\boxed{Au | SnO_2} + K_2SnO_3 \rightarrow \boxed{Au | SnO_2}\ SnO_3K_2$$

$$\boxed{Au | SnO_2}\ SnO_3K_2 \rightleftarrows \boxed{Au | SnO_2}\ SnO_3^{=} + 2\,K^+.$$

Although peptised purple of Cassius behaves in solution as a high molecular complex, it cannot be considered as such because the gold retains its elementary nature. See Chapter V.

Transitional Stages Between Electrolytic Solutions and Irreversible Hydrosols

There are so many transitional stages between solutions of electrolytes and irreversible hydrosols that no sharp dividing line may be drawn. Let us consider an aqueous solution of iron chloride as it is diluted successively. At great dilution a yellowish brown precipitate of ferric hydroxide, or the gel of iron oxide is obtained. It has not yet been determined whether the precipitate is $Fe(OH)_3$ or amicrons of Fe_2O_3 separated from each other by spaces filled with water. For the sake of simplicity we will assume the latter, as van Bemmelen has done, without committing ourselves to either hypothesis.

Iron oxide, or a hydrated oxide, is formed from ferric chloride even in concentrated solutions. At the same time a number of ferrioxychlorides are formed as a result of hydrolysis and dissociation; the constitution and composition of these are not very well known. The amicrons of iron oxide find plenty of cathions to adsorb, and from which they can get the positive charge. The particles do not unite but remain in solution. As the dilution becomes greater more iron oxide is formed and either unites with the amicrons to increase the mass, or goes to form more amicrons which in turn adsorb more cathions. When the dilution has become sufficiently great the majority of the cathions of the ferric chloride, or oxychloride are adsorbed. Further dilution or

the addition of alkali results in the discharge of the colloidal particles because of the adsorption of hydroxyl ions. A similar process comes to pass when a solution of ferric chloride or nitrate is subjected to dialysis.

At higher temperatures the hydrolysis is much more pronounced. Even when the concentration is fairly great a hydrosol may be obtained. Witness the appearance of the brown color on warming a solution of ferric nitrate. Long boiling effects a complete hydrolysis of ferric acetate. Here the conditions are favorable for the formation of large particles, and the amicrons grow into the submicroscopic field. The hydrosols are strongly turbid owing to the presence of meta-iron oxide and the submicrons exhibit a crystalline character, as demonstrated by Cotton and Mouton.

Theory of Membrane Equilibria in the Presence of Electrolytes that Cannot be Dialyzed Out

Donnan * has investigated the equilibria that result when an ionic combination is shut off from migrating electrolytes by a semipermeable membrane.

A. Division of an Electrolyte with a Common Ion. — Assume the complete dissociation of the salt NaR into the ions Na^+ and R^-. The solution is to be separated from sodium chloride solution by a membrane impermeable to the ion R^-. The system may be schematically represented thus:

$$\begin{array}{c|c} (1) & (2) \\ Na^+ & Na^+ \\ R^- & Cl^- \end{array}$$

Sodium chloride would diffuse from (2) to (1) and we should then have the equilibrium:

$$\begin{array}{c|c} (1) & (2) \\ Na^+ & Na^+ \\ R^- & \\ Cl^- & Cl^- \end{array}$$

The work necessary for the isothermal, reversible transportation of one mol of sodium ion from (2) to (1) is exactly equivalent to that work gained by the transportation of one mol of Cl under the same conditions. The total work gained, or the loss of free energy, is therefore zero.

$$\partial n \mathrm{R}T \log \frac{[Na^+]_2}{[Na^+]_1} + \partial n \mathrm{R}T \log \frac{[Cl]_2}{[Cl]_1} = 0,$$

$$[Na^+]_2 \times [Cl^-]_2 = [Na^+]_1 \times [Cl^-]_1, \qquad (1)$$

* F. G. Donnan: Zeit. f. Elektrochemie, **17**, 572–581 (1911).

wherein the brackets represent molar concentrations. Complete dissociation and equal volumes on either side the membrane are assumed.

Original state				Equilibrium					
Na^+	R^-	Na^+	Cl^-	Na^+	R^-	Cl^-	Na^+	Cl^-
c_1	c_1	c_2	c_2	$c_1 + x$	c_1	x	$c_2 - x$	$c_2 - x$
(1)		(2)		(1)			(2)	

c_1 and c_2 are the molar concentrations of the respective ions.

$\frac{100\,x}{c_2}$ is the per cent of NaCl that diffuses from (2) to (1).

$\frac{c_2 - x}{x}$ is the relation of NaCl on the two sides of the membrane at equilibrium.

From equation (1) we have the relation

$$(c_1 + x)\,x = (c_2 - x)^2 \quad \text{or} \quad x = \frac{c_2^2}{c_1 + 2\,c_2}.$$

TABLE 12

Original concentration of NaR in 1. c_1	Original concentration of NaCl in 2. c_2	Original relation of NaR to NaCl, $\frac{c_1}{c_2}$.	Per cent NaCl diffused from 2 to 1, $\frac{100\,x}{c_2}$.	Final distribution relation of NaCl between 2 and 1, $\frac{c_2 - x}{x}$.
0.01	1	0.01	49.7	1.01
0.1	1	0.1	47.6	1.1
1	1	1	33	2
1	0.1	10	8.3	11
1	0.01	100	1	99

From the table it will be seen that in case the concentration of NaR is large in comparison to that of NaCl the latter will scarcely penetrate the membrane. On the contrary, if the concentration of NaCl is very large compared to that of NaR, the latter will scarcely affect the diffusion of the sodium chloride.

B. Osmotic Pressure. — The unequal division of NaCl influences the measurement of the osmotic pressure. Let P_0 be the true osmotic pressure of NaR, and P_1 the observed osmotic pressure. According to Donnan we obtain the following equation:

$$\frac{P_1}{P_0} = \frac{c_1 + c_2}{c_1 + 2\,c_2}.$$

In case c_1 is small compared to C_2, $P_1 = \frac{1}{2} P_0$. On the other hand if c_2 is small compared to c_1, $P_1 = P_0$. In other words the osmotic pressure of the salt that does not penetrate the membrane is unaffected if its concentration is great compared to that of the diffusing salt.

C. Division of an Electrolyte without a Common Ion. — If KCl is substituted for NaCl in the considerations under *A* we come to the following result.

If the concentration of NaR is large compared to KCl, most of the K^+ will diffuse through to (1); only a small amount of Cl^- will go from (2) to (1), and a small part of the sodium will go from (1) to (2). On the contrary, if the contraction of KCl is large compared to that of NaR, an appreciable quantity of Na will go from (1) to (2).

D. Hydrolytic Decomposition of Salts by a Membrane. — If pure water is put on one side, (2), of the membrane and the solution of NaR on the other, (1), the sodium ion has a tendency to go through to (2). This is possible only when the hydroxide ion also diffuses from (1) to (2). The solution in (1) becomes acid while that in (2) must be alkaline. The relations may be represented thus:

Original State			Equilibrium					
(1)		(2)	(1)			(2)	
Na^+	R^-	Pure water	Na^+	H^+	R^-	Na^+	OH^-
c_1	c_1		$c_1 - x$	x	c_1	x	x

From considerations similar to those made in deriving equation (1) we obtain:

$$\frac{[Na^+]_1}{[Na^+]_2} = \frac{[OH^-]_2}{[OH^-]_1} \tag{2}$$

Assuming complete dissociation of the electrolytes and the same volume on each side of the membrane, the following relations obtain for equilibrium:

$$\frac{c_1 - x}{x} = \frac{x}{[OH]_1}.$$

$$x \times [OH^-] = K_w$$

Therefore

$$\frac{c_1 - x}{x} = \frac{x^2}{K_w}, \quad \text{or} \quad x^3 = K_w (c_1 - x).$$

If x is small compared to c_1, then

$$x = \sqrt[3]{K_w \cdot c_1}.$$

Under these conditions the hydrolysis of NaR is very small as evidenced by the following table.

TABLE 13

c_1	x	$\frac{100\,x}{c_1}$
		Per cent
0.01	5.10^{-6}	0.05
0.1	1.10^{-5}	0.01
1	2.10^{-5}	0.002

By increasing the volume of (2) the hydrolysis may be increased.

When $v_2 = 100\,v_1$ and $c_1 = 0.1$, $\dfrac{100\,x}{c_1} = 10^{-1}$.

If the dissociation constant of HR is very small, or the acid very insoluble the hydrolysis will be greater. Donnan has made calculations for several such cases.

E. Ionization of an Acid, the Anion of which Cannot Pass Through a Membrane. — When the pure acid is in the compartment (1) and sodium hydroxide in (2) much of the latter will dialyze from (2) to (1). A non-dialyzable salt will be formed in (1). If the acid was originally in the form of a gel or tiny crystals, it would exhibit no osmotic pressure against pure water. On the other hand, if sodium hydroxide is added to (2) osmotic pressure will be manifested at once. Donnan has calculated the potential differences at equilibrium for several such cases. These calculations are important in considerations concerning the nerves, and for the explanation of the electrical organs in many fishes.

Donnan's theory is also applicable to complex ions having a high molecular weight, where there is little tendency to penetrate membranes.

CHAPTER V

INORGANIC COLLOIDS *

A. Colloidal Metals

General Properties. — Those colloidal metals that are free from protective colloids will be treated first. They occur often in submicroscopical form, have the most varied colors, and are particularly suitable for ultramicroscopic investigation. In spite of this property they may be obtained in a nearly homogeneous form if sufficient care is exercised during the preparation. Under certain circumstances scarcely a ray of light is discernible even under the ultramicroscope. They cannot be prepared in concentrated form, generally under 0.1 per cent. If the endeavor is made to concentrate them either by evaporation, ultrafiltration, or by treatment with electrolytes, coagulation invariably results. They are almost always negatively charged in neutral or very weakly alkaline or acid solution. Under suitable conditions, sometimes, they can be made to separate out at the cathode. Generally, however, any attempt to change their direction results merely in the complete discharge of the particles and the subsequent precipitation of the colloid. In these cases the precipitation laws of Schulze and Hardy hold approximately.

The most characteristic property of this class is the strong tendency among the particles to unite with one another.† In fact the preparation of colloidal metals may be regarded as an interrupted condensation process. This tendency is so pronounced that even energetic dissolution may occasion coagulation. Opposed to this is the property of forming colloidal combinations with protective colloids. The complex has many of the properties and exhibits the reactions of protective colloids. Sufficient weight has not always been given to this behavior in the study of reversible colloids. The fact that metal colloids may imitate the reactions and properties of the protective colloid when only traces of the latter are present, without losing their own optical properties, demonstrates quite clearly the fallacy of the hypothesis which says that the particles of protective colloids are fine and all alike in size. It is equally untenable to consider them as molec-

* Chapters V to IX inclusive.

† R. Zsigmondy: Zur Erkenntnis der Kolloide, 141 (1905).

ular divisions of the nature of crystalloids. For instance, colloidal gold to which gelatin to the amount of 3 per cent of the weight of gold has been added, resembles gelatin in its properties. It can be precipitated by tannic acid but not by table salt. Practical use is made of the above mentioned property in the determination of the protective action of reversible and irreversible colloids toward gold. The determination of the gold number helps to classify the protective colloids. See gold number, page 106.

In spite of the fact that some authors have questioned whether colloidal metals really belong to colloidal solutions, contending that they are in reality suspensions, nevertheless this class has contributed greatly toward our knowledge of the entire field. In addition to what has already been said, Bredig's * article on the analogy between colloidal metals and ferments may be cited. Colloidal metals have been the occasion of many other advances and have stimulated the development of ultramicroscopy. The confirmation of the kinetic theory resulted from Svedberg's † work on the Brownian movement. Moreover Biltz ‡ has shown that the mutual precipitation of colloidal metals with positively charged hydrosols cannot be explained on the assumption of a salt formation; and in general that during the precipitation of colloids, as well as in the case of dyestuffs, chemical and also specific reactions are involved. The synthesis of the purple of Cassius from colloidal gold has been of importance for the theory of colloidal chemistry. The peptisation of this purple has rendered the purely chemical point of view of peptisation untenable. As shown by Lüppo-Cramer § many of the phenomena of photography can be explained on the basis of considerations concerning the behavior of colloidal metals. The photochlorides of Carey Lea have been shown by R. Lorenz and Lüppo-Cramer ¶ not to be subchlorides but adsorption complexes.

Preparation. — Pure metal hydrosols are prepared either by reduction of the corresponding salt in dilute solution, by electric colloidation according to Bredig and The. Svedberg, or by light reactions. For instance, Svedberg || prepared silver hydrosol by the action of ultraviolet light on a silver plate submerged in water. The process is applicable to lead, copper, and tin, but fails with aluminium or gold.

* G. Bredig: Anorganische Fermente. Leipzig (1901).

† The. Svedberg: Studien zur Lehre von den kolloiden Lösungen, 125–160. Upsala (1907).

‡ W. Biltz: Ber., **37**, 1095–1116 (1904).

§ Lüppo-Cramer: Kolloidchemie und Photographie. Dresden (1908).

¶ M. Carey Lea und Lüppo-Cramer: Kolloides Silber und die Photokloide. Dresden (1908).

|| The. Svedberg: Ber., **42**, 4375–4377 (1909); Koll.-Zeit., **6**, 129–136 (1910).

Siedentopf succeeded in making silver bromide hydrosol by means of light through the cardioid ultramicroscope.*

Protected Colloids. — Combinations of metal colloids and protective colloids have often been classed with metal colloids. They will be dealt with later, but are of sufficient interest to warrant a few remarks here. To this class belongs Lea's colloidal silver, and Paal's colloidal metals † that show the interesting catalytic effect in reduction reaction with hydrogen; for instance, the formation of succinic acid from fumaric acid and the preparation of stearic acid from oleic acid.

The practical applications of colloidal metals are many; an instance in point is Kuzel's lamps. Protected metal colloids have been used in medicine but there seems to be a difference of opinion as to their efficacy.

1. Pure Metal Colloids

Conditions for Stability. — Attention must be again called to the sensitiveness toward electrolytes of pure metal colloids, very small quantities of electrolytes sufficing to cause precipitation. The question naturally arises why these colloids are so easily coagulated when those of the albumin type are so stable toward electrolytes. Generally this question is set aside with the reply that colloidal metals more nearly resemble suspensions than do the hydrofiles. The answer, however, does not satisfy, for a small quantity of protective colloid renders colloidal metals just as stable toward electrolytes as albumin is. The degree of dispersion is not changed by the addition of the protective colloid; the particles must increase their size and mass somewhat and therefore more nearly approach the suspensions. Furthermore amicroscopic gold hydrosols are almost as sensitive to electrolytes as those whose particles are much larger. Hence any explanation of electrolyte sensitiveness on the basis of the degree of dispersion is unsatisfactory. Equally untenable is the assumption made by Donnan,‡ to explain the dissolution of colloids, that there is an attraction between the particles and the surrounding medium. A feasible theory offers an opportunity to the theoretical physicist and has not yet been presented. At present we must content ourselves with the hypothesis in accordance with the facts, that the attraction of the particles for one another is great enough to cause an irreversible union if the ultramicrons come sufficiently close together, as they must do during ultrafiltration or centrifugali-

* Page 14.

† C. Paal und C. Amberger: Ber., **37**, 124–139 (1904): **38**, 1398–1405 (1905); **40**, 1392–1404 (1907).

‡ F. G. Donnan: Zeit. f. phys. Chemie, **37**, 735–743 (1901); **46**, 197–212 (1903).

zation. All influences, therefore, that render it more difficult for the particles to come within the critical distance (the distance at which they will unite) tend to make the system more stable. Enumerated these are:

1. The average distance of the particles from one another.
2. The electric charge on the particles.
3. The viscosity of the medium.
4. The union of the metal ultramicrons with protective colloids.

With regard to the effect of 1 on the stability we know from experiment that the stability of gold hydrosol is increased on dilution. This is probably due to the fact that the particles are less likely to come within the sphere of other particles when the distance between them is great. During ultrafiltration, evaporation, and centrifugalization the particles are brought close together and coagulation results. In other words the distance between the particles must not be too small or precipitation takes place in spite of the electric charge.

The influence of discharge of the particles has been dealt with in Chapter IV. In all cases where the particles are discharged coagulation results. The discharge is not confined to the influence of electrolytes, but may be brought about by α rays, ultraviolet rays, etc. In all these cases the precipitation takes place without a necessary change in the distance between the ultramicrons.

The most efficient means of preventing an irreversible union between the particles is the addition of protective colloids. The true significance of this will be considered later. It might be remarked here that there are all possible grades of protective effect. Colloids which give scarcely any protection against electrolytes may prevent the change of color when the hydrosol is concentrated in collodion sacks. It is possible to concentrate a colloidal gold solution to a considerable degree by ultrafiltration without a change of color, where, under similar circumstances, the unprotected colloid would change its color and coagulate.

Colloidal Gold

Preparation and Properties

Colloidal solutions of metallic gold have been known for over two hundred years. Ruby glass has been recognized since the time of Kunkel, 1679, and the gold purple of Cassius since 1685. In both preparations the gold is in the colloidal form, although this fact was not a matter of common knowledge until recent years. Pure gold hydrosols were first made by Faraday * in 1857. Although he did not realize

* Faraday: Phil. Transact., 154 (1857).

the relation of his preparations to ruby glass and the purple of Cassius, the work is so fundamental and important that a short account will be given here. The term colloidal solution was not proposed by Graham until a year later.

Faraday treated dilute gold chloride solutions with phosphorus dissolved in ether or carbon disulfide. From this he obtained more or less turbid solutions, sometimes purple red, sometimes violet or blue. The gold settled out very easily; occasionally, however, the solutions were stable for several months. Faraday set himself to prove that the blue or red constituent of these solutions was metallic gold in a finely divided state. He succeeded in showing that the electrical colloidation of gold in air or hydrogen gave a precipitation on glass or quartz which had the same red or blue color as the gold solutions. He also proved that the precipitate from his solutions behaved exactly like gold. From this he concluded that the precipitate was not a chemical combination of gold. He did not carry out a quantitative analysis. He further allowed the condensed rays of sunlight to pass through the solutions and noted the diffusion of light. Sometimes the color was unmistakably that of metallic gold. He also convinced himself that solutions such as potassium chromate did not give the same diffusion. Faraday did not conclude, as many commenting on his article have since done, that his solutions were coarse suspensions of gold, probably because he continually asked himself the question whether he had succeeded in preparing gold in the molecular form. He considered it astonishing that the volume of the precipitate was several hundred or even thousands of times that which it would be in the more compact metallic form.

The work of Faraday remained unnoticed for over forty years. Even those who were studying ruby glass and the purple of Cassius did not take it into cognizance. The author himself was not familiar with these investigations of Faraday when the former began his work on the nature of the purple of Cassius.

The author * has worked out a method for the preparation of stable solutions of pure colloidal gold. The procedure consists in reducing dilute, slightly alkaline gold solutions at boiling temperature with formaldehyde. The best results are obtained by the following method: 120 cc. of specially distilled water are brought to boiling in a Jena glass beaker. During the heating 2.5 cc. of a solution of $HAuCl_4 \cdot 4\,H_2O$ (6 gms. to the liter) and 3 to 3.5 cc. of a 0.18 normal solution of potassium carbonate are added. As soon as the boiling point has been

* R. Zsigmondy: Liebigs Annalen, **301**, 30 (1898); Zeit. f. analyt. Chemie, **40**, 711 (1901).

reached 3 to 5 cc. of a dilute solution of formaldehyde (0.3 cc. of ordinary concentrated formalin to 100 cc. water) are added with violent shaking or stirring. Soft glass stirring rods are to be avoided. In a few seconds, or at longest one minute, an intense red color appears and does not change on further standing. The water used in this preparation is procured by redistilling water in a silver condenser; a Jena glass receptacle is employed to catch the water from the silver condenser. All the liquids necessary for preparing the gold solutions will keep indefinitely so that one to two liters of the desired solutions may be prepared in one hour's time. They are also very cheap, containing about 4 cents worth of gold to the liter.

In this manner deep red or purple red colloidal gold solutions of great stability are obtained. The particles are generally visible under the ultramicroscope, the size being from 10 to 40 $\mu\mu$. The different solutions prepared by this method will not be exactly alike unless great care is exercised in the preparation of the water. These solutions may be used to determine the gold number of other colloids.

If solutions containing finer subdivisions are desired a much greater dilution is necessary when formaldehyde is employed as the reducing agent. The dilution should be increased to $\frac{5}{100000}$ per cent, but fortunately the concentration may be made 100 times greater by subsequent evaporation. The particles in such solutions are amicroscopic. A much simpler preparation * has been developed which is a combination of the above with the method of Faraday. A gold chloride and potassium carbonate solution is prepared by the above recipe and a few drops of a solution of phosphorus in ether are added. The reducing agent is best prepared by diluting a saturated phosphorus solution in ether to about five times its volume. About $\frac{1}{2}$ cc. of this will be sufficient for the purpose. If the mixture is allowed to stand for several hours it turns blue, brown, or sometimes black. In 24 hours it will have gradually become red, and contains particles too small to be detected by the ultramicroscope. Often not a trace of the light rays may be seen. The red color appears more quickly if the mixture is boiled. The boiling may be continued until all the ether is driven off, and air may be bubbled through to oxidize the phosphorus without causing any change in the hydrosol itself.

A third method,† which makes it possible to procure solutions of particles of almost any desired size, consists in a combination of the two already given. A colloidal solution of the finest subdivision is prepared by the second method. These solutions may be called nuclear

* R. Zsigmondy: Zur Erkenntnis der Kolloide, 100 (1905).

† R. Zsigmondy: Zeit. f. phys. Chemie, **56**, 65–76 (1906).

solutions or nuclear liquids. A second mixture is prepared from potassium carbonate and gold chloride in exactly the same proportions as in the first method. Formaldehyde is now added but before the reduction begins a definite quantity of the nuclear liquid is also added to the hot mixture. It is advantageous to add water so that the reduction without the nuclear liquid would occupy about two minutes. The reduction without the nuclear liquid would take place slowly and the result would be a turbid purple colored solution. When the nuclear solution is added the reduction is almost instantaneous and a clear deep red gold solution is obtained. The size of the particles may be regulated somewhat by the amount of nuclear liquid added, a small amount aiding in the formation of larger particles, while a large amount may leave the ultramicrons still amicroscopic.* It is obvious that the liquids must be free from any substances that would act in a manner detrimental to the nuclear solution.

The explanation of the effect of the nuclear liquid is doubtless that the particles act as centers around which the condensation takes place, just as occurs in the formation of crystals. The individual particles grow in the mixture as long as there remains any gold to be reduced. If there are a great many nuclei present the supply of gold will be exhausted quickly and the particles cannot become so large as they would if few nuclei were added.

Not only may the size of particles in gold solutions be thus regulated in order to obtain solutions for specific purposes, but this same method may also be employed to determine the dimensions of the amicrons in the original nuclear liquid.

The most concentrated solutions made by one or other of these methods contain from 5 to 7.5 mgs. of gold per 100 cc. The volume may be decreased to about one-half, but further decrease of volume usually results in coagulation because of the increasing concentration of the dissolved electrolytes. If more concentrated gold solutions are desired dialysis must be resorted to in order to lessen the amount of electrolytes present. For this purpose the dialyzer should be kept in a warm place where there is a good circulation of air to aid in the evaporation. In this manner it is possible to increase the concentration from 10 to 20 times. The author has succeeded in preparing solutions containing 0.12 per cent of gold by this method. If the concentration is carried far enough shining gold rings may be obtained on the spherical shaped parchment membrane. The gold thus formed will amalgamate slowly with the vapors of mercury.

Colloidal solutions are tasteless and non-poisonous. The gold is

* W. Menz: Zeit. f. phys. Chemie, 66, 132 (1909).

precipitated by a series of bases, acids, and salts. Contrary to the effect of most electrolytes potassium cyanide does not produce coagulation in dilute gold solutions for the reason that it partially dissolves the gold, and consequently makes the color lighter. With more concentrated gold solutions potassium cyanide causes the color to become blue, and precipitation follows. Poorly dissociated electrolytes, such as acetic acid or ammonium hydroxide, have a small precipitating effect.

Other methods for the preparation of gold solutions by chemical means have been proposed from time to time without bringing out anything very new. Gutbier * employed hydrazine, Donau † carbon monoxide, and Doerinckel ‡ hydrogen peroxide as reducing agents. These methods have the advantage that they prevent the possible formation of protective colloids. One might also reduce gold solutions with sugar, phenols, aromatic aldehydes, ethereal oils, etc.; but for many purposes it is inadvisable to introduce foreign substances into the gold hydrosol. Blake § used an ether solution of acetylene to reduce the gold and obtained fairly concentrated solutions which he employed for experiments on coagulation.

An electrolytical method for the preparation of colloidal gold originated with Bredig.¶ An electric arc, about 1 mm. long, between gold points is formed under water. Four to five amperes at 110 volts may be used, but 8 to 10 amperes at 70 volts are more satisfactory. The gold solution thus obtained is blue or violet blue in color and is free from electrolytes. Purple red solutions are made from these preparations by adding a small amount of alkali. Hydrosols prepared by this method are preferable for investigations where the presence of electrolytes would interfere with the measurements, such as the determination of the conductivity, and also where dissolved substances may act as catalytic poisons.

Paal's method for preparing gold solutions involves the use of protective colloids, and will be discussed in the chapter on platinum colloids.

Evidence of the Metallic Nature of Colloidal Gold

While Faraday endeavored to establish by qualitative experimentation that his gold subdivision was metallic gold, the direct analysis was first made on the precipitate obtained from the formaldehyde

* A. Gutbier: Zeit. f. anorg. Chemie, **31**, 448–450 (1902).

† J. Donau: Monatsh. f. Chemie, **26**, 525–530 (1905).

‡ F. Doerinckel: Zeit. f. anorg. Chemie, **63**, 344–348 (1909).

§ J. C. Blake: Amer. Journ. of Sc. (4), **16**, 381–387 (1903).

¶ G. Bredig: Zeit. f. Elektrochemie, **4**, 514 (1898); Zeit. f. angew. Chemie, 951–954 (1898). Anorganische Fermente, 24. Leipzig (1901).

preparation that had been thrown down by sodium chloride.* The precipitate was gathered in an asbestos filtering tube, dried and heated to redness in a current of carbon dioxide. The resulting gas was caught over potassium hydroxide to remove the carbon dioxide, and the remainder treated with pyrogallic acid and phosphorus. These two latter took up only one-tenth as much as they would have if the precipitate had consisted of the lowest oxide of gold, Au_2O. Some nitrogen remained, showing that the gold had adsorbed a small amount of air. Further, aurous oxide, Au_2O reacts with HCl according to the following equation.

$$3\,Au_2O + 6\,HCl = 4\,Au + 2\,AuCl_3 + 3\,H_2O.$$

When the precipitate was treated with hydrochloric acid mere traces of gold went into solution, from which it may be concluded that an extremely small amount of aurous oxide could have been present. Because for other reasons higher oxides of gold could not have been present, it follows that the precipitate must have been metallic gold.

J. C. Blake † prepared colloidal solutions of gold by reduction with acetylene dissolved in ether, and analyzed the precipitate obtained by treatment of the hydrosol with barium salts. He found it quite pure or contaminated with a very small amount of barium if the precipitate was thrown down in alkaline solution. There were also traces of carbon which doubtless came from the ether.

A few words may be added with regard to purple gold oxide, the existence of which had already been doubted by Proust, Buisson, Figuier, and definitely negated by Kreuss.‡ The assumption was made to explain the color of ruby glass and the purple of Cassius at a time when colloidal solutions of gold were not known.

Theory of the Color of Colloidal Gold

The color of colloidal gold solutions in transmitted light may be red, violet, or blue, and occasionally yellowish brown, or brown. The ultramicrons of red solutions are green; those of blue solutions are yellow to reddish brown; violet solutions contain both. We have therefore to do with green, yellow, or brown ultramicrons. There is not the multiplicity of colors here that there is in the case of silver solutions.

Relations Between Color and Size of Particles.—Both green and brown ultramicrons may have all possible dimensions from the amicro-

* R. Zsigmondy: Liebigs Annalen, **301**, 43 (1898).

† J. C. Blake: Contributions from the Kent Chem. Lab. of Yale University, CXX., 4 Ser, 16 (1903)

‡ G. Kruess: Liebigs Annalen, **237**, 274–307 (1887).

scopic to 120 $\mu\mu$ and over. As a general thing, however, the large particles are yellow or brown while the very fine subdivisions are green. At present there is no explanation for the fact that very small particles are sometimes brown. Nevertheless the following may be the key to the situation. According to Mie's theory particles of gold having a diameter of 40 $\mu\mu$ and under must be green. The assumption is thereby made that the shape is spherical and the particle a compact mass of metallic gold. Any divergence from the theory may mean that the conditions are not fulfilled. In other words when the very small particles are brown, either the shape is not spherical or the entire space occupied by ultramicrons is not filled with metallic gold. The first assumption does not seem to be entirely necessary. It may also be contended that the divergence from the theory is due to allotropic modifications of gold. The assumption is quite unnecessary for the explanation of the color and in certain cases leads to contradictions.

With regard to the brown color of very small particles a large number of experimental facts point to the assumption that the ultramicrons are not composed of massive gold. For instance, whenever the green particles become flocculent, or approach very close to one another, the color changes to brown, even when the aggregate is still amicroscopic. It would seem therefore that small brown particles are in reality conglomerates of the green. Green ultramicrons, on the other hand, are composed of compact gold, and are the result of the normal growth of amicroscopic particles, or better, perhaps, they are tiny crystals.

The assumption that the particles are spherical in form is made solely for the purposes of calculation, and a number of facts would seem to discredit the hypothesis. The very great independence of the color on the diameter makes it seem plausible that ultramicrons in red hydrosols are not necessarily spherical when the size is 40 $\mu\mu$ and under.

Absorption Spectra. — The absorption spectra of red gold solutions were found to correspond well with that of ruby glass first by the author and since by many other investigators. In deep red or purple red solutions the maximum absorption lies near the spectral line *E*. In the case of blue gold solutions the maximum lies nearer the red end of the spectrum. The absorption band is also wider, and the refracted light from the particles is yellow or brown.

Brown Gold Hydrosols. — Beside blue violet and red gold subdivisions there exist others that appear yellow or brown in transmitted light. These have long been known to chemists. Very often during the preparation of the purple of Cassius from $SnCl_2$ and $HAuCl_4$ brown liquids are obtained that gradually become red. Similar results are frequently met with in the reduction of dilute gold chloride solutions

by phosphorus. Gold ruby glass containing a considerable quantity of lead or tin often solidifies to a dark yellow or brown mass. The author has prepared yellowish red liquids by the reduction of very dilute solution of gold chloride with formaldehyde. Recently Svedberg * fundamentally investigated these liquids. Whether the color is due to the particles of gold in the water or glass, or whether it is a result of conglomerates of gold and PbO, SnO_2, P, etc., cannot at present be decided upon. That the brown color usually appears when foreign bodies are present such as an excess of phosphorus in the reduction of gold chloride, speaks in favor of the assumption that conglomerates cause the brown color.

Theory of the Colorations. — A great many thorough investigations exist on the theory of the colorations in colloidal metals.† Ehrenhaft explains the color on the assumption of an optical resonance of the particles. Maxwell Garnett has calculated the absorption spectra of gold hydrosols and ruby glass by means of Lorenz's theory ‡ for optical inhomogeneous media, and has found that the results agree very well in many respects with those obtained by direct measurement. The agreement is, however, only partial. For instance, Maxwell Garnett calculated the absorption curve for gold solutions having molecular dimensions (dissolved crystalloid) and found a maximum at

$$\lambda = 0.475\,\mu.$$

According to this even a crystalloid solution of metallic gold must be colored. Rapidly cooled ruby glass which contains metallic gold is, however, colorless. The objection to this that the gold is in chemical combination with the glass is untenable, for the glass remains colorless on rapid cooling regardless of the presence of a large excess of reducing agent, which latter must have freed all the gold from combination.

A theory that explains a large number of experimental facts has been proposed by Mie. Where the growth of the particles has been normal in the gold solutions the polarization, absorption spectrum, and the diffusion of light all agree well with the theory. Mie gives a complete presentation of the integration of Maxwell's formula for a sphere and the induction of a sphere by a direct, linear polarized light wave. The absorption in the gold solution is calculated from the loss of energy that the wave experiences in the sphere, and that is made up of the

* The. Svedberg: Zeit. f. phys. Chemie, **65**, 624–633 (1909); **66**, 752–758 (1909); **67**, 249–256 (1909); **74**, 513–536 (1910).

† F. Ehrenhaft: Sitzungsber. d. Akad. d. Wiss. Wien, **112**, 11a, 181–209 (1903); **114**, 11a, 1115–1141 (1905). F. Kirchner und R. Zsigmondy: Drudes Annalen d. Phys. (4), **15**, 573–595 (1904).

‡ L. Lorenz: Wiedemanns Annalen, N. F., **11**, 70–103 (1880).

loss through heat and diffusion of light. The absorption coefficient is calculated by multiplying the energy loss on one particle by the number of particles.*

The absorption coefficient for dilute solutions with very small particles is according to Mie.†

$$K = NV\frac{6\pi}{\lambda'} \cdot Im\left(\frac{n_0^2 - n_1'^2}{2n_0^2 + n_1'^2}\right).$$

N is the number of particles in a cubic centimeter; V is the volume of a particle; λ' is the wave length in water; n_0 is the refractive index of water; and n_1' is the complex refractive index of the gold. The symbol Im signifies that the imaginary part of the complex expression is to be taken. For larger subdivisions the refraction coefficients a, b, c, d must be added. The above is an approximation formula, for a, b, c, d become equal to unity when the particles decrease sufficiently in size. It has been shown that the absorption curve is the same for all solutions of gold where the concentration remains constant and the particles are not very large. This agrees very well with the facts, for gold solutions differ little in color where the particles lie between 1 and 40 $\mu\mu$, provided that the growth has been normal, and the particles have not been formed by the union of two or more others as in coagulation.

According to Mie, Rayleigh's formula obtains for the diffusion of light by gold solutions having very small particles.

$$N\frac{24\pi^3V^2}{\lambda'^4} \cdot \left|\frac{n_0^2 - n_1'^2}{2n_0^2 + n_1'^2}\right|^2,$$

where the symbols have the same significance as before and the vertical lines indicate that the absolute value of the expression must be taken. For larger particles a, b, c, d must be introduced. The value of the term inside the vertical lines outweighs that of the well-known factor in Rayleigh's formula, so that the curve for gold solutions differs from that of isolated particles calculated from Rayleigh's formula.

From the formula in the above paragraph it may be concluded that the curves for different sized particles are similar, and that the ordinates, where the gold concentration is the same ($N\ V$ is a constant), are proportional to the volumes of the particles. This agrees fairly well with the experimental facts.

From Fig. 16 which was constructed from measurements by Steubing,‡ it will be seen that the diffusion of light is only a fraction of the absorption, and that the former becomes smaller with decrease in the

* F. Hasenoehrl: Sitzungsber. d. Akad. d. Wiss. Wien, **111**, **11a**, 1229–1263 (1902).

† G. Mie: Koll. Zeit., **2**, 129–133 (1907).

‡ W. Steubing: Drudes Annalen d. Phys. (4), **26**, 329–371 (1908).

size of the particles. While the absorption of liquids having ultramicrons with a diameter of 36 or 20 $\mu\mu$ is almost the same, there is a marked difference in the intensity of the diffusion. The latter is small for particles of 20 $\mu\mu$ and is immeasurable at 2 to 4 $\mu\mu$.

Optically those gold solutions with small amicrons behave exactly as homogeneous solutions of dyestuffs. A part of the absorption is to be attributed to diffusion of light only when the subdivision of the gold is much coarser. The diffusion in the larger subdivisions has an appreciable influence on the color. In the case of the finer subdivisions of gold hydrosols the color is not a question of the color of a

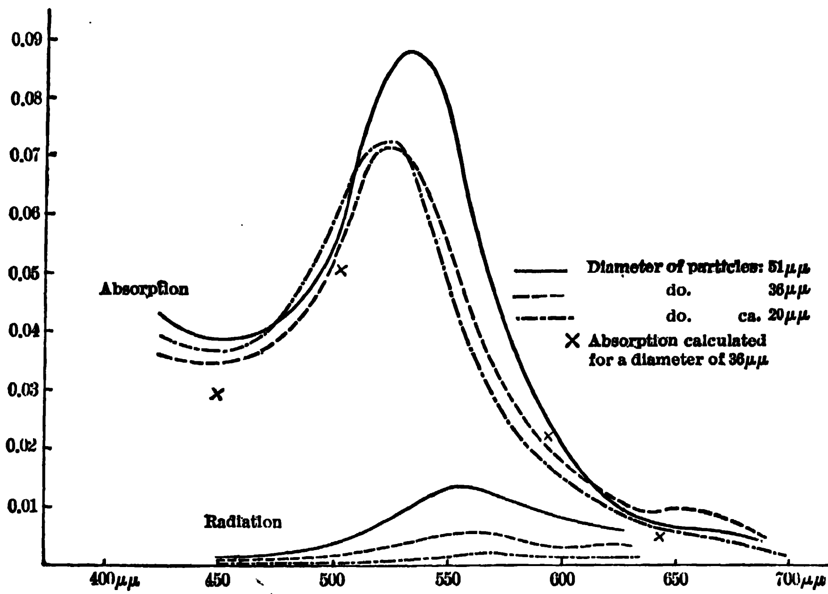


FIG. 16. Absorption and radiation per cc. of a 0.0025% red gold solution.

turbid medium, such as the blue of the heavens, as has been wrongly assumed by many, but is rather a specific absorption of ether waves that may be calculated from the optical constants of the metal.

Polarization by the Particles.—Light from the side is polarized by the ultramicrons. The smaller the particles the more complete is the polarization, and this is linear, not elliptical. Diagrams 17 and 18 are taken from an elaborate article by Mie * on the relation of the size of the particles to the polarization. The figures hold for direct rays of sunlight. The intensity of the diffracted light is represented by the length of the radial vectors from the particles. The outer curve cuts off portions of the radial vectors that are proportional to the total

* G. Mie: Drudes Annalen d. Phys. (4), **25**, 429 (1908).

radiation. The inner curve gives the same thing for the nonpolarized light. The portion between the two curves is, therefore, proportional to the polarized light. The arrows show the direction in which the ray is traveling.

From the figures it will be seen that the very small gold particles diffract light, that the latter is completely linear polarized in a direction at right angles to the path of the ray, and that in all other directions the light is only partially polarized.

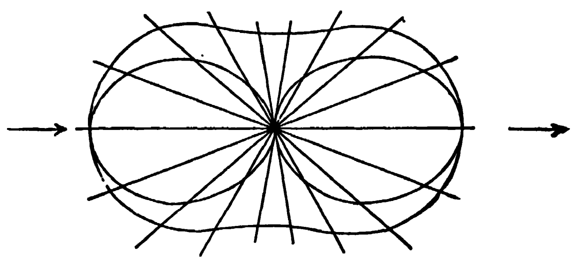


FIG. 17. Radiation diagram of an "infinitely" small gold particle.

On the other hand, particles of 160 $\mu\mu$ and over give a maximum polarization at 120 degrees, and send much more light in the direction in which the ray is traveling than in any other.

The theoretical optics of metal colloids anticipates many phenomena that are found in practice. A special instance is the color and the polarization of particles produced by normal growth. On the contrary,

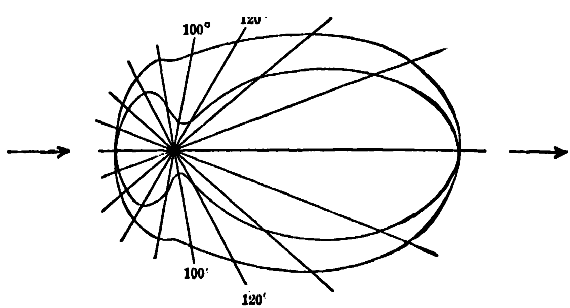


FIG. 18. Radiation diagram of a gold particle having a diameter of 160 $\mu\mu$.

a complete explanation of many other phenomena is wanting; especially the change in the color during coagulation to a yellowish or reddish brown, regardless of whether the particles are amicroscopical or submicroscopical. There are many facts that go to show that the ultramicrons are not isodimensional in their contour, but are long and flat or leaf shaped. For instance the dichroism of gold gelatin films *

* The. Svedberg: Arkiv för Kemi, 4, No. 19 (1911).

must be attributed to a difference in the distance between the particles in the two directions, or to a definite orientation of tiny rods or leaves differing lengthwise of the film from that which they have at right angles to the film. The last is the more probable because all gold hydrosols are not suitable for showing dichroism with gelatin and the property is manifested in a marked degree only by those containing anisotropic particles. Experiments by the author with gold solutions of definite amicrons failed to show any dichroism. It might also be noted that gold often crystallizes in a leaf-like form having six sides and that Ambronn * has observed dichromatic microscopic rods.

A strong argument that the color of the ultramicrons is determined by their form is offered by the experiments of Siedentopf.† When gold or silver ultramicrons are pressed between the cover glass and the platform of the cardioid ultramicroscope the green or variegated particles become brown. The color change may be caused by the pressure on small cubes as well as by the orientation of tiny flakes or rods. Similar results were obtained by pressure on sodium chloride particles colored with sodium. The change of color here is doubtless due to the pressure on the submicrons, causing them to assume another form.

If we assume a flattening effect by pressure on the particles, or an orientation of the flakes or rods such that the largest surface is at right angles to the pressure, we may represent the results in the following scheme,‡ Table 14.

If the light vibrations from the polarizer are parallel to the shorter diameter of the particles, that is, at right angles to the flat side, then transmitted light is red and diffracted green.

If, on the contrary, the vibrations are parallel to the larger surface and at right angles to the shorter, then the transmitted light is blue and the diffracted yellow or brown.

TABLE 14

Direction of pressure.	Supposed position of particles.	Plane of vibration.	Direction of observation.	Color of NaCl in transmitted light.	Color of NaCl in reflected light.
—	0	—	.	Red	Green
—	0	1	.	Blue	Orange brown
|	o	—	.	Blue	Orange brown
|	o	1	.	Red	Green
.	0	—	.	Blue	Orange brown
.	0	1	.	Blue	Orange brown

* H. Ambronn: Zeit. f. wiss. Mikroskopie, **22**, 349–355 (1905).

† H. Siedentopf: Verh. d. Deutsch. Phys. Ges., **12**, 6–47 (1910).

‡ *Ibid.*

In complete accord with these ideas are the observations of Ambronn and Zsigmondy* on the pleochroism of silver or gold gelatin films, for which the first named offered the explanation. Anisotropic metal particles (flakes or rods) are similarly oriented by the spreading out of the gelatin. If the vibrations of the transmitted light are parallel to the distention direction of the gelatin the color is blue. If the vibrations are at right angles to the distention, the color will be red. The orientation of the submicroscopic rods or flakes of gold is such that the longest diameter is parallel to the direction of the strain. This is to be expected if one supposes the particles to occupy small spaces that will be stretched by the distention. From these considerations it follows, as Siedentopf has pointed out, that the theory of Mie must be expanded to include rotation ellipsoids.†

Change of Color During Coagulation. — What has been said in the foregoing paragraphs does not suffice to explain all the phenomena encountered. A characteristic property of all pure red gold solutions is the change to blue during coagulation. This change is occasioned by the union of two or more particles that diffract green. The complex thus formed diffracts only brown light waves. It is impossible to explain the color change on the grounds of an increase in the size because it occurs regardless of whether amicrons or submicrons unite. In the first of these cases the complex may still remain amicroscopic and have a mass several hundred times smaller than that of a large red particle. Nevertheless these tiny complexes diffract brown and the liquid appears blue.

It seems necessary to assume that the particles unite to form a somewhat loose flocculent mass, and do not melt into one another as drops of liquid do. For if the latter were the case the color would be the same for all particles of the same substance having like dimensions. However, as already stated, there is no relation between size and color unless the growth has been normal; that is, not caused by union of several ultramicrons larger than molecules.

There is another important conclusion to be drawn from the considerations discussed in the foregoing, *viz.*, that a decrease in the surface is not a very prominent factor in the coagulation. Even if one assumes that the liquid films between the particles are broken the decrease of surface must be confined to the edges or faces that touch.

A reversible change of color may be brought about by evaporating a

* H. Ambronn: Ber. d. Kgl. Sächs. Ges. d. Wiss. Leipzig, 48, Math. phys. Kl., 613–628 (1896).

† H. Siedentopf: Verh. d. Deutsch. Phys. Ges., 12, 32 ff. (1910). O. Wiener. Phys. Zeit., 5, 332–338 (1904).

colloidal gold solution with a very small amount of gelatin.* The dried residue is blue while the color changes to red if moisture is added. The change of color has been explained by Kirchner † on the basis of Plank's ‡ dispersion theory for isotropic dielectrics. He regards the particles as resonators that, on coming into close proximity with one another, displace the absorption maximum toward the red end of the spectrum, at the same time causing a widening and increased intensity of the maximum. This is borne out very well in practice. Mie § has raised objections to Kirchner's theory so that a satisfactory elucidation is not yet at hand. A complete optical theory of metal colloids must unquestionably explain the change of color that is so characteristic of gold and other metal colloids.

Siedentopf ¶ has observed an unmistakable dichroism of gold gelatin films when viewed at an oblique angle. He assumes that the change of color on drying is due to a change of form of the particles and not to the distance between them. It is difficult to conceive of a reversible change of form, however, and it seems much better to assume an orientation of the particles parallel to the distention surface of the film. But this cannot be the only factor involved in the change of color on dry desiccation, because the color of the residue seen through a Nichol's prism suitably placed is a turbid violet red and differs greatly from the deep red obtained by the addition of moisture. The distance between the particles must play a part here just as it does in the coagulation of gold solutions.

A word may be added with regard to blue gold hydrosols. The blue obtained on the reduction of gold chloride solutions may be attributed to three causes. First, the reduction may be incomplete and colloidal gold oxide be formed instead of gold.|| Further reduction, perhaps at higher temperatures, might cause the blue to change to red. This condition has not been taken cognizance of up to the present time. Secondly, the reduction may be complete and the blue color be attributed to the flocculent union of particles already spoken of; or perhaps to the irregular growth so that, instead of flakes or needles, husk-shaped bodies are called into being. These of course may be

* F. Kirchner und R. Zsigmondy: c. Drudes Annalen d. Phys. (4), **15**, 573–595 (1904); R. Zsigmondy: Zur Erkenntnis der Kolloide, 114 (1905).

† F. Kirchner: Ber. d. Kgl. Sächs. Ges. d. Wiss. Leipzig, 54, Math. phys. Kl., 261–266 (1902).

‡ M. Planck: Drudes Annalen d. Phys. (4), **1**, 69–122 (1900); Sitzungsber. d. Klg. Akad. d. Wiss. zu Berlin (1902), 470–494.

§ G. Mie: *l. c.* page 98.

¶ H. Siedentopf: Verh. d. Deutsch. Phys. Ges., **12**, 36 (1910).

|| R. Zsigmondy: Zur Erkenntnis der Kolloide, 114, 133–134 (1905).

submicroscopic. Finally, the liquid may contain large massive gold particles that, according to the theory of Mie, would account for the blue color.

The Behavior of Colloidal Gold under the Influence of a Fall of Potential

Under the influence of a potential fall dialyzed and concentrated gold solutions behave differently from freshly prepared hydrosols that contain electrolytes. In both cases the particles migrate toward the anode; a phenomenon that is easily demonstrated in Coehn's apparatus, as described on page 47. If, however, the electrodes are dipped into non-dialyzed gold solutions the migration is not easily seen. Frequently there is no precipitation on the anode, or at least the amount is inappreciable. Instead, most of the gold sinks to the bottom in the form of red clouds, and occasionally there is an accompanying change of color. The cause for this lies in the fact that acids or free halogens are generated at the anode, the charge on the particles is changed, and these start off toward the cathode.* Some of the particles are now charged positively while others are still negative. The two charges neutralize each other, and the particles unite to form electrically neutral combinations that fall out of solution. If chlorine is evolved at the anode it partially dissolves the gold to form gold chloride.

With well dialyzed or concentrated solutions a precipitation of the gold on the anode in the form of a black powder may be obtained.† This black powder after it has been dried has the glance of gold. Here traces of impurities may act as protective colloids, and no precipitation occurs on the anode, but instead a concentration in the anode portion may take place. The author was enabled to observe such a condition of affairs during the electrolysis of gold solutions containing gelatin.

Galecki ‡ has recently carried out elaborate investigations on the electrical migration of gold particles. He found in confirmation of the work of Blake and Svedberg § that increased additions of electrolytes gradually discharged the particles, and that the system became unstable in the region of the isoelectric point. He found further that the mobility of the particles under a given potential difference was in-

* J. Billitzer: Zeit. f. phys. Chemie, **45**, 307–330 (1903). J. C. Blake: Zeit. f. anor. Chemie, **39**, 72–83 (1904).

† R. Zsigmondy: Liebigs Annalen, **301**, 36 (1898).

‡ A. v. Galecki: Zeit. f. anorg. Chemie, **74**, 174–206 (1912).

§ Chapter III, page 49.

dependent of their size, but appreciably affected by the accidental presence of electrolytes. In general the mobility increases after dialysis. The absolute rate of migration of the particles in a well dialyzed hydrosol may reach that of the chloride ion.

Reactions of Colloidal Gold

The gold in hydrosols amalgamates very incompletely or not at all with mercury. A well dialyzed or concentrated gold solution suffers no perceptible change after two or three days' shaking with mercury. If the experiment is kept up for several weeks with frequent shaking there is often in specific cases a change in the shade of the solution, and an increase in turbidity may be noted. The cause of this is doubtless the dissolution of the mercury to form an electrolyte, and the consequent partial coagulation of the hydrosol. This phenomenon has not been studied with the ultramicroscope. Precipitated colloidal gold and the purple of Cassius behave similarly. It should be noted that Berzelius took the fact that the purple of Cassius would not unite with mercury to indicate that the purple was a combination of gold oxide with tin oxide.

On account of the negative charge the gold particles are particularly sensitive to the precipitating action of cathions. Because trivalent ions have a more intense effect than bivalent, and the bivalent greater than univalent, extraordinarily small amounts of trivalent cathions precipitate gold from colloidal solutions. Excess of aluminium salts may cause a reversal of sign and form a stable positively charged hydrosol. Dyestuffs, such as Fuchsin, Bismarck Brown, etc., that migrate toward the cathode, precipitate gold with the accompanying change of color and are carried down with it. After the precipitate has settled out the liquid is often colorless. The dyestuff cannot be dissolved out by water but can be extracted with alcohol. The residue is in the form of a black powder. Likewise, positively charged colloids, such as iron oxide, aluminium hydroxide, zirconium oxide, etc., precipitate the gold as has been shown by Biltz. Definite quantity relations must be maintained, however, in order to precipitate completely both colloids. Table 15 * represents these relations for colloidal gold and iron oxide solutions.

Similar relations hold for gold fuchsin precipitation; an excess of either leaves the liquid colored. The position of the optimum depends upon the concentration of both solutions, upon the state of subdivision of the gold, and upon some other factors.

* W. Biltz: Ber., 37, 1104 (1904).

TABLE 15

10 cc. of gold solution containing 1.4 mg. Au were mixed with 5 cc. of iron oxide solution, the concentration of which varied.

Fe_2O_3 mg.	Observations.	
	Immediate.	After one hour.
8.0	No precipitation	Large flocks settled slowly
4.0	Formation of flocks, very slow settling	Same as above
3.2	Complete precipitation	Complete precipitation, liquid colorless
2.4	Large flocks, slow precipitation	Same as above
1.6	Flocks, solution red	Flocks, solution rose color
0.8	Fine clouds, very slow precipitation	Flocks, solution rose color
0.32	No precipitation	Very slight turbidity

Adsorption of Colloidal Gold by Aluminium Hydroxide, Fibers, and Barium Sulfate

Of interest is the adsorption of colloidal gold by substances such as dissolved dyestuffs. This property depends less upon the surface of the metal than it does upon the degree of subdivision of the gold, that is upon the number and size of the particles. A typical case is the adsorption of gold by aluminium hydroxide. When the hydroxide and the gold solution are shaken together the former becomes more or less intensely red, just as it does when shaken with Carmine Red. In both cases under suitable circumstances the liquid is rendered colorless. In the one case a carmine lacquer, and in the other a lacquer like combination of gold and hydroxide is obtained. The formation of the gold lacquer can be followed under the ultramicroscope. Gold solutions and fibers affect each other in a similar manner.*

Gold and Barium Sulfate. — A number of fine crystalline precipitates, such as calcium carbonate, strontium carbonate, and barium sulfate, also have the property of adsorbing gold particles. The last-named reaction was discovered by Vanino,† who showed that barium sulfate may be used in this way with a number of irreversible hydrosols. In an account of an investigation not published he demonstrated that only the smaller particles of the barium sulfate have the property of uniting with the gold. The amount of sulfate necessary to remove the color from 5 cc. of the gold solution depends upon quality

* R. Zsigmondy: Verh. d. Ges. D. Naturf. u. Ärtze, 73 Vers., 171. Hamburg (1901). W. Biltz: Nachr. d. Kgl. Ges. d. Wiss. zu Göttingen, Math.-phys. Kl., 18–32 (1904); Ber., **37**, 1095–1116 (1904).

† L. Vanino: Ber., **35**, 662 (1902).

of the barium sulfate. Of a preparation purchased 21 to 60 mgs. were necessary to decolorize completely 5 cc. of a gold solution containing 0.25 mg. of gold. After the addition of a sufficient quantity of protective colloid no decolorization by the sulfate could be observed. There is a lower concentration limit of the protective colloid under which the precipitation is not prevented. In the case in point the lower limit with 5 cc. of the above gold solution and 60 mgs. of barium sulfate is as follows:

Glue	0.1 mg.
Gum arabic	0.044
Albumin	0.5 to 1.5

If less than these amounts of protective colloids are added the gold is completely coagulated. On the other hand an excess produced a white precipitate leaving a red liquid that contained the gold and the protective colloid. When both the sulfate and the protective colloid are increased complications arise. There may be a partial coagulation of both the gold and the protective colloid, or both may be adsorbed by the sulfate.

Protective Effect and the Gold Number

The sharp change of color makes gold solutions particularly well adapted for demonstrating the effect of protective colloids. These solutions served to demonstrate for the first time that protection was a general property of reversible and also some irreversible colloids, and that chemical reactions were not necessarily involved.* The change of color by electrolytes in red gold solutions is prevented by protective colloids, but the specific members of the class differ markedly in their effect. We have at hand, therefore, a means of further characterizing this group of substances. This is done by means of the gold number.

By the gold number we will understand the maximum number of milligrams of protective colloid that may be added to 10 cc. of gold solution without preventing a change of color from deep red to violet shades by 1 cc. of a 10 per cent solution of sodium chloride, where the change would take place if no protective colloid were added.

For the determination of the gold number hydrosols prepared by the formaldehyde method having particles lying between 20 and 30 $\mu\mu$ are the most suitable. The correct degree of subdivision may be known by a faint brownish opalescence in incident light; in transmitted light the solution must be deep red and clear. If the protective effect of the colloid in question is approximately known, it is wise to dilute until a few tenths of a cubic centimeter will prevent the

* R. Zsigmondy: Zeit. f. analyt. Chemie, 40, 697–719 (1901).

color change. If the effect is quite unknown it should be roughly determined before accurate measurements are attempted.

0.01, 0.1, and 1 cc. of the solution to be determined (*a*, *b*, and *c*) are put into three small beakers and thoroughly mixed with 10 cc. of gold solution. At the end of three minutes 1 cc. of a 10 per cent sodium chloride is added to each and the contents well mixed. Assuming that there is a color change in (*a*) but not in (*b*) nor (*c*), the gold number must lie between 0.1 and 0.01. For more accurate determinations 0.02, 0.05, and 0.07 cc. of the protective colloid should be taken and the procedure repeated. Where the color is not sharp interpolation between unquestioned concentrations must be resorted to.* From the following table it will be gathered that the gold number varies greatly, and can therefore be used to characterize this class of substances.

TABLE 16

Colloid.	Gold number.	Reciprocal gold number.	Class of protective colloid.
Gelatin and glues	0.005–0.01	200–100	I
Isinglass	0.01–0.02	100–50	I
Casein	0.01	100	I
Gum arabic, good	0.15–0.25	6.7–4	II
Gum arabic, poor	0.5–0.4	2–0.25	II
Sodium oleate	0.4–1	2.5–1	II
Tragacanth	2 (about)	0.5 (about)	III
Dextrin	6–12 10–20	0.17–0.08 0.1–0.05	III
Potato starch	25 (about)	0.04 (about)	III
Silicic acid	∞	0	IV
Aged stannic acid	∞	0	IV
Slime from the kernel of quince	∞	0	IV

In the table the reciprocal gold numbers make the comparison more striking. The results are reproducible provided the same gold solution is employed under the same conditions. For this reason it is possible to detect a change in the gold solution by this method, although the changes of state in the gold solutions do not have so great an influence as the differences in the quality of the protective colloid.† An example of how the gold number may be employed to distinguish between protective colloids was worked out jointly with Schulz in Jena. The white of a hen's egg may be separated into different portions by fractional precipitation with ammonium sulfate.‡ The individual

* R. Zsigmondy: Zeit. f. analyt. Chemie, **40,** 697–719 (1901).

† Fr. N. Schulz und R. Zsigmondy: Hofmeisters Beiträge z. chem. Physiol. u. Pathol., **3,** 137–160 (1902).

‡ *Ibid.*

fractions are not distinct chemical bodies, nevertheless they have certain characteristics.

The first fraction contains globulin, then follows crystallized albumin and finally amorphous albumins mixed with ovomucoids. Ovomucoid has the peculiar property of not coagulating when the slightly acid egg solution is boiled, and can therefore be isolated. Globulins are insoluble in pure water but require a certain amount of salt before they will go into solution. The gold number of globulin lies between 0.02 and 0.05 while that of the ovomucoids lies between 0.04 and 0.08.

The individual albumin fractions differ very greatly. The first fraction obtained by the presence of ½ per cent sulfuric acid separates out in the form of microscopic crystals, some of which are well defined. After several recrystallizations the gold number remained constant between 2 and 8. In order to obtain these constant gold numbers it is necessary to recrystallize more often than is usual in physiological chemistry. The next albumin fraction is amorphous and has the striking property of turning the gold solution turbid and blue or violet without the aid of an electrolyte. The third fraction is likewise amorphous and in contradistinction to the second fraction exercises a high degree of gold protection. The gold number was determined in the normal way and lay between 0.03 and 0.06. Although the three fractions of albumin had similar chemical properties, yet they showed marked differences toward gold solutions.

Zunz * has made similar observations in the case of albumoses. As is well known albumoses are decomposition products of egg albumin and are produced during digestion. They are more closely related to albumin than are the peptones, and manifest great differences in diffusion in that primary albumoses diffuse with difficulty while the secondary albumoses diffuse easily. The primary albumoses are more easily precipitated by ammonium sulfate than are the secondary. To the primary albumoses belong heteroalbumoses soluble only in dilute salt solutions, protalbumoses soluble in pure water, and synalbumoses. The gold numbers found by Zunz * for the three decomposition products are as follows:

Heteroalbumoses	0.01 to 0.075
Protalbumoses	1.6 to 3.36
Synalbumoses give violet color at	0.64 to 2.24

The synalbumoses have no protective action on gold solutions but act in a manner very similar to the second albumin fraction. Zunz† has re-

* E. Zunz: Archives internat. de Physiol., 1, 427–439 (1904).
† E. Zunz: Bull. Soc. Roy. des Sc. med. et nat., 64, 174–186 (1906).

cently investigated the behavior of a series of secondary peptones and albumoses toward gold solutions and found that all have the property of turning the color from red to blue, but that they possess this property in a varying degree. The principal results are set forth in Table 17.

TABLE 1

Substance.	Smallest amount of substance in mgs. that will suffice to turn 10 cc. colloidal gold solution violet.	Substance.	Smallest amount of substance in mgs. that will suffice to turn 10 cc. colloidal gold solution violet.
Thioalbumoses.......	2.60–4.00	Albumoses B......	0.70–1.80
Albumoses A........	2.24–3.20	" B.....	0.80–2.80
" B........	0.08–0.32	" C.....	1.60–3.20
" B........	0.20–0.80	Peptone..........	0.24–0.52
" B........	0.50–1.40	"	3.60-7.40
" B........	0.40–1.20	"	4.40–8.20
" B........	0.80–1.60		

Zunz * found further that there is no relation between the effect of albumoses and peptones on gold solutions and the change of the surface tension of the water through these substances.

TABLE 18

Substance.	Concentration.	Gold number.	Number of drops in stalagmometer, 100 drops distilled water taken as standard.
	Per cent.		
Heteroalbumoses...........	0.1	0.01–0.075	114.4
Protalbumoses..............	0.1	1.6–3.36	113.0
Synalbumoses..............	0.1	Causes color change	113.7
Egg albumin................	1.0	About 0.1-0.3	105.5

From the table it will be seen that albumin changes the surface tension very little, while the albumoses cause a very appreciable change. Again the albumoses vary enormously in their effect on gold solutions, while their change of surface tension of the water is almost identical, as seen from the stalagmometrical measurements.

In a later article Zunz † has pointed out that there is no relation between the effect of the albumoses on mastic solutions and the effect on gold solutions. Heteroalbumoses and synalbumoses precipitate mastic turbidities, while other albumoses do not. On the other hand heteroalbumoses have a protective action on gold solutions.

* E. Zunz: Bull. Soc. Roy. des Sc. med. et nat., **64,** 187–203 (1906).
† E. Zunz: Arch. internat. de Physiol., **5,** 111, 245–256 (1907).

From what has been said it will be seen that the electric charge on the particles is not the only factor involved. For if this were the case both gold and mastic solutions should be affected in a similar manner, as they are both negative. Rather must the action be attributed to specific properties that have not yet been clearly explained.

The gold number has also been employed to determine whether or not changes have taken place in protective colloids as a result of standing or of temperature variations. It has been demonstrated that the protective property decreases in intensity with the lapse of time. This decrease may be caused by partial coagulation, as well as by chemical changes such as hydrolysis, decomposition, etc. A number of colloids possess a different gold number at boiling point from that at the temperature of the room.

A systematic investigation of the change of state in gelatin solutions has been carried on by Menz * at the instigation of the author. Concentrated gelatin solutions harden to jellies whereby numerous large submicrons are formed. In more dilute solution the same changes take place but the ultramicrons formed are smaller the more dilute the solution. It can be easily seen from the following table that the protective effect is greater the more dilute the solution; that is the gold number is smaller the smaller the ultramicrons are.

TABLE 19

Concentration of gelatin solutions in the cold.	Gold number.	
	One day old.	Constant some days later.
Per cent.		
1	0.037	0.039
0.5	0.023	0.025
0.1	0.015	0.016
0.01	0.014	0.015
0.001	0.0065	0.012

The gelatin particles in a 1 per cent solution are so large that they may be seen with the ultramicroscope. It is remarkable that the large particles as well as the small ultramicrons unite with the gold, and that the reaction may be followed under the ultramicroscope. Contrary to the action of the small particles, where probably several of the gelatin particles unite with one gold ultramicron, the large gelatin particles take up many gold particles. This happens at the same time as a gradual change of color toward the purple and an increase in the turbidity of the gold gelatin mixture. Should the concentration of the

* W. Menz: Zeit. f. phys. Chemie, 66, 129–137 (1909).

gelatin be high enough the gold gelatin clouds fall to the bottom. In spite of this the gelatin has had a protective effect and sodium chloride causes no change of color toward the blue if sufficient gelatin is present.

It is not uninteresting that protective colloids are present in normal urine, and that these behave much as gelatin does. That is to say the degree of subdivision increases on boiling, whereby the protective effect is increased. These relations were discovered by Lichtwitz and were studied by him in collaboration with Rosenbach.* These colloids in urine usually escape observation because their protective effect is overshadowed by the precipitating influence of the dissolved electrolytes. By dialysis, shaking out with benzine, or by precipitating the protective colloid with alcohol according to Salkowsky,† the colloid may be separated from the most of the electrolyte, when the protective effect may be demonstrated. The gold number of these bodies lies between 0.3 and 1.2. It is a noteworthy fact that the increased protective action of the urine colloids is associated with the property of the urine to prevent the precipitation, on cooling, of the uric acid sediment formed by the boiling. Such samples of urine, the gold number of which has not changed on boiling, allow the uric acid sediment to precipitate immediately on cooling; while those the protective action of which is increased from 1 to 10, or 1 to 5, prevent the precipitation wholly or at least partially.

Of general interest is the observation that urea, uric acid, urochrome, hippuric acid, and hypoxanthin have no protective action, while nucleinic acid is a protective colloid having a gold number 2.5. Urine albumin does not always operate as a protective colloid.‡ The cause is probably to be sought for in the size of the particles, which latter may be seen under the ultramicroscope as established by the work of Ræhlmann, Much, Romer, and Siebert.§

Theory of the Protective Action

On the basis of an elaborate investigation the author ¶ has expressed the opinion that the protective action is due to the union of several ultramicrons of the protective colloid with a particle of the gold; or vice versa, the gold particles are adsorbed by a protective individual.

* L. Lichtwitz und O. Rosenbach: Hoppe-Seylers Zeit. f. physiol. Chemie, **61**, 112–118 (1909). L. Lichtwitz: *Ibid.*, **64**, 144–157 (1910). O. Rosenbach: Inaug.-Diss. Göttingen (1909).

† Salkowsky: Berl. klin. Wochenschr., Nr. 51–52 (1905).

‡ L. Lichtwitz: Hoppe-Seylers Zeit. f. physiol. Chemie, **72**, 215–225 (1911).

§ E. Raehlmann: Munch. med. Wochenschr., Nr. 48 (1903). H. Much, P. Roemer und C. Siebert: Zeit. f. diät. u. phys. Therapie, **8**, 19–27, 94–96 (1904–5).

¶ R. Zsigmondy: Verh. d. Ges. D. Naturf. u. Ärtze., 168–172. Hamburg (1901).

Several other hypotheses have been made. For instance Bechhold,* Neisser and Friedemann † have attributed the prevention of the precipitation of bacteria and suspensions by protective colloids to a homogeneous encircling of the suspended particle. While this explanation may be accepted without hesitation for the case of coarser suspensions, it is not satisfactory for protected ultramicrons whose dimensions are in the neighborhood of the molecular. The individual particles of the protective colloid must have a certain size, and the protection is greater the smaller the protected ultramicrons. In order that a particle of gold might be completely surrounded by a larger gelatin particle, the latter would of necessity have liquid properties. This assumption is not borne out by any evidence and is doubtful in the extreme. See Chapter XII on the ultramicroscopy of gelatin.

Neisser and Friedemann also believed that only oppositely charged particles could have a protective action. This point of view is also contrary to fact, for particles of like charge often have a much greater protective action than those of opposite charge. Because of this fact Billitzer ‡ concluded that the particles of the protected and the protective colloid do not unite at all, but that the protective colloid adsorbs the precipitating electrolytes. This is also untenable because a good protective colloid will offset the action of a million times its own weight of a precipitating electrolyte. It seems much more in accordance with the fact to assume a mutual adsorption as already explained in the author's hypothesis in the foregoing paragraph. As early as 1900 the author demonstrated that gold foil adsorbed gelatin and covered itself with a layer that could not be removed by boiling water. This layer prevented the amalgamation of the gold with mercury. The experiment turns out better if the surface of the gold foil is roughened by repeated amalgamation and redissolving of the mercury.

Direct evidence for the union of the particles was obtained by noting the dependence of the protective effect upon the concentration and the time occupied by the reaction. If the protective effect is not due to the mutual action of the particles of the two colloids upon each other, then it should be practically instantaneous as soon as the mixing is complete. Experiment shows, however, that several minutes are often necessary before the protection is complete.§ The time is doubtless taken up in formation of the union between the particles. The concentration of the protective colloid when it is added to the

* H. Bechhold: Zeit. f. phys. Chemie, **48,** 385–423 (1904).

† M. Neisser und U. Friedmann: Münch. med. Wochenschr., **51,** 465–469, 827–831 (1903–4).

‡ J. Billitzer: Zeit. f. phys. Chemie, **51,** 129–166 (1905).

§ R. Zsigmondy: Zeit. f. analyt. Chemie, **40,** 713 (1901).

gold solution plays an important part. For instance, $\frac{15}{1000}$ mg. of gelatin dissolved in 3 cc. water have a protective action on 10 cc. of gold solution if let stand 10 minutes before adding more water, amounting to 20 cc. If, however, the 20 cc. are added to the gelatin solution before mixing with the gold solution there is no longer a protective action. It is evident from this that it is not the presence of the gelatin that gives the protection, but the action of the gelatin on the gold particles. After the protective action has once set in further dilution does not counteract it. All this speaks for the union (adsorption) of the particles. Moreover the union of the particles can be followed directly in the ultramicroscope when the particles of the protective colloid are large enough. Such observations have been made in the case of colloidal aluminium hydroxide and gold solution, and also gelatin and gold. When the particles of the gelatin are large enough, the second type of protective action is manifested, *viz.*, the adsorption of several gold ultramicrons by a particle of gelatin.

The mutual adsorption of the ultramicrons results in the gold hydrosol losing its characteristic properties, *viz.*, irreversible dehydration and sensitiveness to electrolytes, while the complex particles assume the properties and show all the reactions of the protective colloid. If the protective colloid can be precipitated by a given reagent, so can the gelatin gold complex. On the contrary if the protective colloid is unaffected by the electrolyte in question, the complex will also be exempt from the influence.

From these considerations some interesting conclusions may be drawn with regard to the nature of protective colloids. For, if the complex particles, consisting of one large gold individual and several smaller gelatin ultramicrons, have the same properties in solution as the pure gelatin, then these properties must be practically independent of the size of the particles, or, in other words, of the state of subdivision. In point of fact the larger subdivisions of gelatin have almost identical properties with the finer. On the other hand it should be noted that the above law is not altogether of general application. There are cases where the gold particles do not entirely lose their power to unite. In such instances it is possible to separate the gold from the excess of the protective colloid by fractional precipitation, and the first fraction then usually exhibits reversible properties. Just as in the case of many chemical reactions the addition of another molecule causes a complex formation whose properties differ from those of the original molecules, so in this case also two different bodies unite, and the resulting complex has properties differing from either of the original components. Contrary to the pure chemical reactions we do not have to do here with

new bodies of constant composition. The laws of definite or multiple proportions are not involved, and the complex may have some of the properties of one or both components. It is important to note that these colloidal complexes exist whose reactions may imitate those of pure chemical substances, because this has led to many misunderstandings and wrong conclusions.* As an example of another case may be cited the adsorption of colloids by fibers. Here again the reactions so nearly resemble those truly chemical that misconceptions are liable to arise.

B. Colloidal Platinum

Colloidal platinum has been prepared by Lottermoser † in a chemical way by reduction with formaldehyde, by Gutbier ‡ using phenylhydrazin, and by Bredig § by means of electrical colloidation. When well prepared the solution is a brown, faintly turbid liquid containing sometimes as high as 20 mgs. of platinum per 100 cc. This hydrosol is renowned because of its excellent catalyzing properties. It contains ultramicrons differing in size from 30 to 50 $\mu\mu$, which refract light somewhat less than gold or silver particles. They are generally colored greyish white shading into yellow or blue. They possess, in a high degree, the property of compact platinum to catalyze the decomposition of hydrogen peroxide. This property has been thoroughly studied by Bredig and his students, and by many other investigators. The reaction is interesting because, as Bredig has pointed out, there is remarkable analogy between it and that of blood corpuscles, enzymes, and ferments. For this reason Bredig has called his hydrosols "anorganische Fermente," although colloidal platinum does not manifest many specific fermentation effects. Many substances, such as hydrocyanic acid, hydrogen sulfide, etc., greatly reduce or totally destroy the catalytic effect of both the ferments and the platinum solutions. Bredig, in conjunction with his collaborators,¶ has carried out a great many series of experiments on the catalytic effect of platinum hydrosols, the most important results of which are given below.

Catalytic Effect. — It was first shown that exceedingly small amounts, one gram mol. of platinum in seven million liters of water, served to increase perceptibly the rate of decomposition of hydrogen peroxide.

* R. Zsigmondy: Zur Erkenntnis der Kolloide, pages 56–61 (1905).

† A. Lottermoser: Anorganische Kolloide, 33 (1901).

‡ A. Gutbier: Zeit. f. anorg. Chemie, **32**, 347–356 (1902).

§ G. Bredig: Anorganische Fermente, 30. Leipzig (1901). Zeit. f. Elektrochemie, **4**, 514–515 (1898).

¶ G. Bredig: *Ibid.* Bredig und R. Müller von Berneck: Zeit. f. phys. Chemie, **31**, 258–353 (1899). Derselbe und K. Ikeda: *Ibid.*, **37**, 1–68 (1901). Derselbe und W. Reinders: *Ibid.*, **37**, 323–341 (1901).

If the concentration of the platinum solution is decreased in geometrical proportion from 2 to 1, the reaction constant decreases from 3 to 1. The reaction is of the first order, although the constant decreases considerably during the reaction. The rate is increased by small amounts of alkali, but large amounts retard it. It is noteworthy that the effect of alkalis on platinum and enzyme solutions is very similar, as shown by Fig. 19.

The change of rate between 25 and 85 degrees was determined and the temperature coefficient (for 10 degrees) was found to be 1.7 for dilute acetic acid solution. The platinum solution must not be warmed too long before the experiment, especially at the higher temperatures, else the activity of the catalyzer is lessened. This is probably due to the partial coagulation of the particles. Warming for 1½ hours at 65 degrees reduced the rate in the relation of 24 : 15. Schoenbein * has observed like effects by the warming of enzymes.

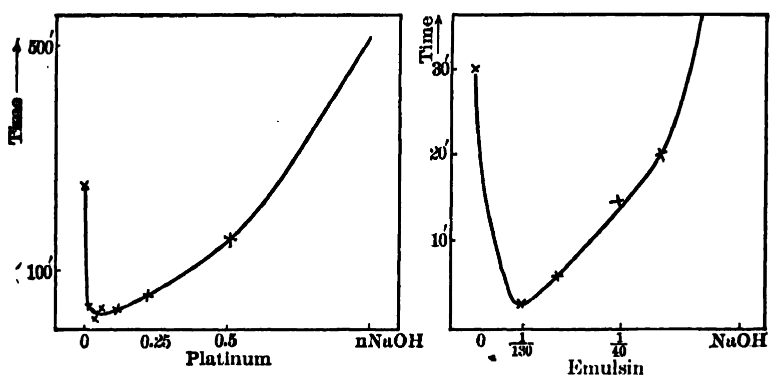


FIG. 19. Effect of alkali on the catalysis.

Poison Effects on Platinum Sols. — Very striking is the singularity that a series of poisons largely prevent or completely destroy the catalytic property of platinum or gold hydrosols. Mere traces of hydrocyanic acid, hydrogen sulfide, arsenious acid, or phosphorus produce an effect. One mol. of hydrogen sulfide in ten million liters of water retarded the reaction measurably. Schoenbein found the same thing to hold for aqueous extractions of potato peelings, and the leaves of Leontodon Taraxacum. The activity of these solutions is instantly retarded by hydrogen sulfide. Bredig found a further analogy between platinum and ferment catalysis in the poisoning by hydrocyanic acid. One mol. of hydrocyanic acid in 20 million liters of water is sufficient to reduce the catalytic action to one-half its former value.

* C. F. Schoenbein: Journ. f. prakt. Chemie (I), 89, 340 (1863).

Schoenbein found that organic materials having the property of decomposing hydrogen peroxide lose this power temporarily when treated with hydrocyanic acid. He suggested that the poisonous effect of this acid on the blood was due to the reduction of the power of the red corpuscles to activate chemically the oxygen of the air breathed.

Both in the case of ferments and platinum sols the catalytic power is revived, although somewhat slowly. The cause for the renewing is probably the oxidation of the poison by the hydrogen peroxide. This latter substance is a well-known antidote for hydrocyanic acid poisoning in the human body. As might be expected from these considerations the poisoning effect on platinum sols is much less if hydrogen peroxide is present when the poison is added. This is also true for enzymes.

Phosphorus is also a poison for platinum, and 0.00004 of a mol. is sufficient to retard the action to one-eighth its value. The relations in the case of carbon monoxide are peculiar. Shaking platinum with this gas stops the reaction almost entirely in about one-half hour. Then a recovery sets in and the catalysis is more vigorous than it was before the poisoning. On the other hand, if hydrogen peroxide is present in excess when the platinum is treated with the carbon monoxide the catalysis is increased from the beginning. To explain this remarkable phenomenon it has been suggested that the carbon monoxide first poisons it and then further subdivides it while the oxidation of the poison is going on. It may be, however, that the carbon monoxide simply removes other retarding substances.

Corrosive sublimate in a dilution of one mol. in two and one-half million liters of water retards the catalysis enormously, and the platinum does not regain its former power. Mercuric cyanide has a much weaker retarding action on both bacteria and platinum solutions.* The far-reaching analogy between the poisoning of organic materials and platinum solutions makes it seem probable that poisoning effects are due to the retarding of catalytic reactions by foreign bodies.

C. Colloidal Silver

It is not by any means so easy to obtain colloidal silver free from electrolytes as it is platinum and gold. Colloidal silver without the presence of some protective colloid is usually in the form of coarser subdivision. In most cases it also contains some silver oxide.

Bredig's Colloidal Silver. — Colloidal silver free from electrolytes can be best made by Bredig's † method of electrical colloidation. The

* Th. Paul und B. Kroenig: Zeit. f. phys. Chemie, **21**, 414–450 (1896).

† G. Bredig: Anorganische Fermente, 31. Leipzig (1901).

hydrosols obtained are usually somewhat turbid, and have a grey or reddish color. Under the ultramicroscope these solutions, as well as those made by other methods, are very beautiful. Bluish red, purplish, or violet stars may be seen moving about with great rapidity in the liquid. When only one sort of colored submicrons is present, blue, for instance, the liquid in transmitted light has almost the complementary color, that is yellow or brown. Because there are a great many different colored particles in the hydrosols prepared by Bredig's method the liquid is a combination of all these and appears grey. Frequently one color predominates even in these solutions prepared by electrical colloidation. Silver solutions containing only amicrons so small that the light cone can scarcely be seen, are usually intense brown in reflected light.

Colloidal Silver by Kohlschütter's Method. — Kohlschütter * discovered another very good method for preparing colloidal silver; *viz.*, the reduction of silver oxide in water by hydrogen. At a temperature of 50 or 60 degrees silver oxide is reduced with the simultaneous formation of a mirror and a hydrosol. The reduction takes place on the walls of the vessel and not in the liquid itself. Strange to relate the color of the sol depends upon the nature of the walls without there being any question of the solubility of the glass, as far as can be ascertained. Walls composed of soft glass or quartz give yellowish brown hydrosols while Jena glass gives red, reddish brown, violet, or blue. With platinum walls no sol formation takes place, but instead crystalline silver separates out. The platinum becomes charged with hydrogen and this replaces the silver in AgOH just as an ordinary metal would. It is a remarkable fact that quartz and ordinary glass have the same effect while Jena glass is totally different. To show that the solubility of the glass was not the vital factor Kohlschütter extracted ordinary ground glass with water and used this solution in conjunction with Jena glass to reduce the silver hydroxide. The resulting hydrosol had exactly the same color that was obtained by the use of Jena glass alone. It is obvious therefore that the surface of the glass has a vital rôle to play in the form and size of the particles.

Silver hydrosols may be purified to a considerable extent by treatment with hydrogen in platinum vessels. The conductivity was reduced to about one-tenth its former value, and had at the end about three times the conductivity of the water employed for the preparation. $K = 4$ to $8 \cdot 10^{-6}$. The purified sol still contained some silver hydroxide. It may be safely assumed that the adsorbed hydroxyl ion insures the stability of colloid and that this ion accounts for the charge

* V. Kohlschütter: Zeit. f. Elektrochemie, 14, 49–63 (1908).

on the ultramicrons. The purification with hydrogen is very useful, because dialysis frequently results in coagulation. It is noteworthy that the unpurified sol contains considerable adsorbed silver hydroxide, which later may be precipitated with the colloid by potassium nitrate. This silver hydroxide can scarcely take part in the conductivity because that of the unpurified hydrosol corresponds to the amount of oxide remaining after the precipitating of the colloid. Most of the silver hydroxide can be reduced by hydrogen without any appreciable change in the color of the hydrosol. The amount of the absorbed oxide is greater in the brown hydrosols than in the variegated, and it is probable that the total silver surface is greater in the former.

D. Other Colloidal Metals

All metal hydro- and even organosols may be prepared by a method worked out by Svedberg * in which the colloidation occurs by means of sparks from an induction coil. With suitable apparatus and carefully purified ethyl ether-pentane, etc., as disperse media colloidal alkali and alkaline metals were obtained. Table 20 gives a comparison between the colors of ether sols of alkali metals, varying in degree of dispersion, and the vapors of the metals themselves.

TABLE 20

Metal.	Color of the ethylethersol.		Color of the vapor of the metal.
	Small particles.	Large particles.	
Li....................	Brown	Brown	....
Na....................	Purple violet	Blue	Purple
K.....................	Blue	Blue green	Blue green
Rb....................	Greenish blue	Greenish	Greenish blue
Cs....................	Blue green	Greenish blue	....

The absorption maximum of colloidal sodium changes from yellowish green to red during coagulation, just as in the case of gold. The stability of the organosols diminishes from sodium to cæsium. Svedberg has also investigated the preparation and the stability of other metal colloids (Mg, Cu, Cd, Hg, etc.) especially in isobutyl alcohol.

Protected Metal Colloids

Every pure metal colloid may be transformed into a reversible colloid by the addition of a protective colloid. Generally the reduction of the metal is achieved in a solution containing the protective colloid;

* The. Svedberg: Ber., 38, 3616–3620 (1905). Studien zur Lehre von den kolloiden Lösungen. Upsala (1907).

or the reduction is allowed to take place under such circumstances that a protective colloid is produced simultaneously with the reduction of the metal, as in the case of Lea's colloidal silver.

Lea's Colloidal Silver. — In 1889 Carey Lea * published an account of his observations on a modification of metallic silver soluble in water. The article did not attract much attention at the time although it opened up a new and very interesting field. It was indeed remarkable that a metal the insolubility of which had been known for ages could be made in a form soluble in water. It was true, of course, that the allotropic silver, as Lea called it, could not be prepared pure, but contained only 97 to 98 per cent silver. The remainder consisted of a colloidal combination of citric acid and iron.

Lea produced his allotropic silver (*A*) by treating in the cold 200 cc. of a 10 per cent silver nitrate solution with a mixture consisting of 200 cc. of 30 per cent ferrous sulfate, 250 cc. of a 40 per cent sodium citrate solution, and 50 cc. of a 10 per cent sodium carbonate solution. The violet precipitate was filtered and washed in water. In order to remove the impurities the precipitation was repeated a number of times with ammonium nitrate. Finally the solution was evaporated and a mass with a metallic luster obtained that consisted mostly of silver. Lea found that the metal did not diffuse through membranes and that it could be freed by this means from electrolytes. Because of these properties and also because inorganic colloids were considered to be allotropic modifications of the metals in question, Lea decided that his silver must also be an allotropic form. Even today we are not in a position to deny this assertion. Barus and Schneider † have shown that it is not at all necessary to assume allotropic modifications in order to explain the subdivision in water or the behavior of the colloid toward electrolytes. We have therefore no direct evidence that the metal in the colloidal state is not an allotropic modification; but the assumption is quite unnecessary and perhaps improbable. On the other hand recent work has shown that allotropy is not so uncommon as it was previously supposed, and if the rule proposed by W. Oswald holds, that the more unstable form appears first, it may very well be that colloidal metals contain, or are, allotropic modifications.

The experiments of Lea were repeated by Prange ‡ a year later. He varied Lea's method for the preparation and found that good silver hydrosols do not show the Tyndall effect. It was wrongly concluded

* M. Carey Lea: Amer. Journ. of Sc. (3), **37**, 476–491 (1889).

† C. Barus und E. A. Schneider: Zeit. f. phys. Chemie, **8**, 278–298 (1891).

‡ J. A. Prange: Receuil d. travaux chim. des Pays-Bas, **9**, 121–133 (1890); J. B., 634 (1890).

from this by Stoeckl and Vanino * that the polarization of the light by the colloidal solution was circular. Later observations have shown that the polarization is always completely or partially linear and never circular nor elliptical. Prange's experiments and also those of Lea † merely show that silver hydrosols, like those of gold, may be obtained in a form that is optically homogeneous.‡

Prange's solutions contained about 0.4 gm. silver in the liter, and were extremely sensitive to electrolytes. Even quartz and graphite coagulated the solutions, during which there was a considerable evolution of heat.

Schneider§ purified his silver hydrosols according to the method of Lea except that he used alcohol to precipitate the colloid. He also showed ¶ that silver organosols such as alcosol and glycerosol could be prepared. He obtained the alcosol by dialyzing the hydrosol with absolute ethyl alcohol, and also by precipitating the hydrosol with somewhat dilute alcohol. The residue was then partially dried on porous plates and finally dissolved in absolute alcohol. In this manner wine red and also chlorophyl green sols may be prepared that show interesting reactions in organic media. Schneider || demonstrated that nonelectrolytes could coagulate alcosols as is clearly set forth in the following table.

TABLE 21

Effect of different substances added to a 0.3 per cent silver alcosol

Instantaneous coagulation.	No coagulation.
Isopropyl alcohol	Propyl alcohol
Primary and secondary butylalcohols	Isobutyl alcohol
Trimethyl alcohol	Cetyl alcohol (in alcoholic solution)
Heptyl alcohol	Glycerin
Octan, formaldehyde	

Silver hydrosols prepared by Lea's method exhibit peculiar reactions that deserve further elucidation. Alkali sulfates, nitrates, and citrates precipitate soluble silver, while iron, nickel, and magnesium sulfates, and barium or silver nitrates, throw down silver that is insoluble in water. The insoluble form may sometimes be peptised with borax and ammonium sulfate, but these reactions are not always reproducible, and it often happens that the repetition gives totally unexpected results.

* K. Stoeckl und L. Vanino: Zeit. f. phys. Chemie, **30**, 98–112 (1899).
† M. Carey Lea: Zeit. f. anorg. Chemie, **7**, 341 (1894).
‡ Sven Odén.: Zeit. f. phys. Chem., **78**, 682–707 (1912).
§ E. A. Schneider: Ber., **25**, 1281–1284 (1892).
¶ E. A. Schneider: *Ibid.*, 1283 (1892).
|| E. A. Schneider: Zeit. f. anorg. Chemie, **7**, 339 (1894).

Of the many remaining forms of silver Lea's golden yellow modification deserves a word. It is obtained by mixing two solutions *a* and *b*. *a* contains 200 cc. of a 10 per cent silver nitrate solution, 200 cc. of a 20 per cent Rochelle salt solution, and 800 cc. of distilled water. *b* contains 107 cc. of a 30 per cent ferrous sulfate solution, 200 cc. of a 20 per cent solution of Rochelle salt, and 800 cc. of distilled water. The second solution must be prepared immediately before use and is added to the first with constant stirring. A glittering red precipitate falls out that gradually becomes black, but looks like bronze on the filter. It is washed and then spread out on a watch glass or dish to dry. The residue forms into lumps that resemble gold. If it is allowed to dry on glazed paper the residue looks like gold leaves. On glass it dries to a beautiful gold mirror. If the washing is carried on too long the color takes on a bronze tone. The preparation is almost 99 per cent silver. It is insoluble in water, and shows a number of very interesting reactions. Oxidizing agents, alkali sulfates, and dilute solutions of potassium ferricyanide cause beautiful interference colors. Pressure changes it to normal silver having the characteristic silver color. When the preparation is impure the color is sometimes black. Warming changes it into light colored silver, and oxidizing agents then fail to produce the interference colors. Long continued treatment with light, electricity, or shaking produces the same effect as pressure. Samples of gold-colored silver that had traveled over 2000 miles loose in a small vessel turned to white silver en route, while other portions of the same sample packed tightly with cotton remained unchanged.* These circumstances as well as the microscopic observations of Ambronn † on the spontaneous transition of silver crystals speak very strongly in favor of the existence of allotropic modifications.

Crystallization. — Lea set aside some of his unpurified red solution in a stoppered bottle for some weeks. At the end of that time a crystalline precipitate was found on the bottom that under a magnifying glass appeared to be short black needles and thin prisms. On the addition of water the form of the crystals was changed, but they did not dissolve. When the mixture was dried a glittering green mass remained. The observation of Lea is of interest because it indicates that the larger ultramicroscopic particles grow at the expense of the smaller until macroscopic crystals are formed. The change of the crystals by water is probably due to enclosed substances soluble in water. This behavior resembles to a certain degree that of crystal-

* M. Carey Lea: Kolloides Silber und die Photohaloide. Deutsch von Lüppo-Cramer, 100. Dresden (1908).

† H. Ambronn: Zeitschr. f. wiss. Mikroskopie, **22**, 349–355 (1905).

-lized egg albumin and the zeoliths which also distend in pure water. Furthermore Ambronn* has succeeded in forming exceedingly thin microscopic crystals that exhibit a pleochroism similar to that of the silver gelatin complex. These crystals sometimes underwent a change by which isotropic crystals were formed.

The growth of gold or silver particles in a suitable reducing mixture is well known, but it has not yet been found possible to cultivate gold crystals by this method. The tendency of silver colloid to form crystals is much more marked, and is probably due to its greater solubility. In a silver sol prepared according to the method of Lea and left standing for about 9 months the author was able to detect a number of glittering crystals with the aid of the microscope.† They were mostly tiny stars with three or six rays resembling snowflakes, and had a diameter of as much as $\frac{1}{4}$ mm. in some cases. Contrary to the experience of Lea, however, these crystals did not distend in water. A spongy mass of silver in water contained an enormous number of tiny crystals after standing for several months.

Technical Colloidal Silver

Technical colloidal silver, such as Argentum Credé, used for medicinal purposes was formerly prepared by a method similar to that of Lea. "Collargol," the much more stable preparation at present procurable on the market, contains an organic protective colloid. Lottermoser and v. Meyer ‡ investigated these technical preparations and found that electrolytes precipitated the first variety; also that alkali and alkaline earth salts of those acids forming insoluble silver salts precipitated the silver in a form insoluble in water. On the other hand alkali salts of those acids that form soluble silver salts precipitated the silver in a soluble form. Chlorides of the heavy metals changed the silver to silver chloride. These authors also found to their surprise that glue, albumin, rubber, etc., prevented the precipitation of the silver by the electrolyte. Today we know, of course, that this is a general property of protective colloids.

Medical Uses. — Colloidal silver is used for intravenous injection, or it is made into a salve for external application in the case of acute rheumatism, pneumonia, pyæmia, etc. As to its medicinal effects the medical world is somewhat divided. Wolfrom § has pointed out that

* *l. c.*

† P. P. von Weimarn: Koll.-Zeit., **5**, 62 (1909).

‡ A. Lottermoser und E. v. Meyer: Zeit. f. prakt. Chemie (2), **56**, 241–247 (1897); **57**, 540–543 (1898).

§ G. Wolfrom: Münch. med. Wochenschr., **56**, 1377–1382 (1909).

the varying experiences may be due to the differences in the preparations employed. Only the preparations of very fine subdivision are efficacious, not the coarser subdivisions. Wolfrom especially lauds its beneficial effects in pus cocci infection, in angina, and also in many cases of infection at the joints.

In support of the contention that it is the very fine subdivisions that are efficacious for medicinal purposes, Henri found that many bacilli are retarded in their growth by finer subdivisions of silver sols even at a dilution of 1 to 50,000, but that the coarser had little effect. The effect of collargol is probably to be attributed to the formation of silver ion at the great dilution. As the ion particles are removed more could be formed from the submicrons present by chemical influences, such as oxidation, etc. The colloidal silver would therefore act for a long time as a storehouse for the ions. The ions would not be present in large enough concentration to injure the tissues. However the cause of the therapeutic effect may lie beyond this. The silver may excite the organism to form antibodies, or cause an increase of metathesis.

Colloidal Metals According to the Method of Paal

Paal and Amberger,* with the help of protective colloids, have succeeded in preparing colloidal solutions of the platinum group, Pt, Os, Pd, Ir. These will be collectively dealt with. The same protective colloids, *viz.*, sodium salts of protalbinnic and lysalbinnic acid, were employed, as in the case of colloidal gold and silver. Reversible colloids of great stability containing as much as 50 to 70 per cent metal were thus obtained. They are not precipitated by even 10 per cent sodium chloride solution but may eventually be thrown down if the concentration of the electrolyte is increased sufficiently. Some of these solutions are not at all precipitated by calcium chloride. Acids, on the other hand, throw down a precipitate soluble in water or in dilute alkalis. The color of the solutions is generally dark brown or black. Paal and his collaborators have carried out some very interesting reactions with these metal colloids that deserve further mention.

Preparation. — The preparation of colloidal platinum according to the method of Paal will be discussed as an example. The sodium salt of lysalbinnic acid is dissolved in three times the amount of water and 2 grams of hydrogen platinic chloride dissolved in water are added. Enough sodium hydroxide is added to unite with the chloride. The

* C. Paal und C. Amberger: Ber., **37**, 124–139 (1904); Journ. f. prakt. Chemie (2), **71**, 358–365 (1904); Ber., **38**, 1398–1405 (1905); **40**, 1392–1404 (1907).

reddish brown liquid so obtained is next treated with hydrazine hydrate. Nitrogen is evolved and after standing for about 5 hours the solution is dialyzed. It is then evaporated on a water bath and eventually in vacuum. The residue is a black, brittle, lustrous mass soluble in water.

Paal and Ambronn have also tried other mixtures and instead of lysalbinnic acid have employed the sodium salt of protalbinnic acid. Colloidal palladium was easily obtained by this method. The evaporation took place at 60 to 70 degrees and the dehydration over sulfuric acid in vacuum. The residue consisted of black, easily soluble lamellæ. The concentration of the metal can be achieved by precipitating with acetic acid, redissolving in sodium hydroxide, and subsequent dialysis. Similarly colloidal osmium and iridium may be prepared. The last-named was made by the use of sodium amalgam as the reducing agent. Osmium colloid cannot be obtained free from oxide unless the dried residue is further reduced by the use of hydrogen at 30 to 40 degrees. The dried residue gradually loses weight owing to the formation of volatile osmium tetroxide.

Colloidal Palladium. — Palladium hydrosol is a brown liquid, at times almost black, and contains for the most part amicroscopic particles. A small portion passes through a collodion filter that will retain dilute hemoglobin solutions, showing that the particles are extremely small. The color of the filtrate is almost the same as dilute solutions of the original liquid, although sometimes the color is a trifle more reddish. Dilute solutions at a concentration of 0.0005 per cent palladium are still colored in layers more than 1 cm. thick, and have a pronounced catalytic action.

Colloidal Palladium Containing Hydrogen. — A palladium hydrogen complex may be prepared from ordinary palladium, palladium black, and also colloidal palladium by both wet and dry methods. In a dry way * it is made by conducting hydrogen over solid colloidal palladium at 60 to 110 degrees whereby three atoms of palladium take up about one atom of hydrogen. By heating to 130 or 140 degrees the hydrogen may be driven off with a current of carbon dioxide without damaging the solubility of the residue. It is a well-known fact that the palladium hydrogen complex is a good reducing agent. In a very fine state of subdivision it is pyrophoric. The hydrosol has been made by Paal and Gerum † by treating the pure palladium hydrosol with hydrogen. It has been found that colloidal palladium will take up from 926 to 2952 volumes of hydrogen, while according

* C. Paal und C. Amberger: Ber., **38**, 1399 (1905).

† C. Paal und J. Gerum: Ber., **41**, 805–817 (1908).

to Mond, Ramsay, and Shields * palladium black adsorbs only 873 volumes. The amount of hydrogen obtained by heating is less than that adsorbed.

Catalytic Properties of the Platinum Group in a Colloidal State

Very interesting are the investigations of Paal in collaboration with Amberger,† Gerum,‡ and Roth § on the catalytic effect of the hydrosols of this group, especially the activation by hydrogen. The effect of the different hydrosols on the decomposition of hydrogen peroxide was determined and the results indicate that the series is

$$Os > Pt > Pd > Ir.$$

A previous treatment with hydrogen may increase the effect very greatly. This was first discovered in the reduction of nitrobenzol whereby a considerable quantity of aniline was formed by the palladium hydrogen complex. This property is not possessed by palladium black nor palladium foil. In order to compare the effect of the different hydrosols the amount of hydrogen used for reduction in the unit of time was calculated. From this could be calculated the volume relations between the activating hydrogen and the palladium. By "Aktivierungzahl" the authors understand the amount of hydrogen in cubic centimeters used by one cubic centimeter of Pd in one hour. This number varied from 12,000 to 32,000 and increased with the temperature. It also depended very largely upon the state of the colloid; old preparations seemed to work better than freshly prepared samples. It is remarkable that aniline can be made by this method, because Bredig found that it is a poison for catalyzers. The explanation is that aniline is at first a poison but in larger quantities has an accelerating effect.

The experimental conditions were that 10 cc. palladium sol, 2 gms. nitrobenzol, and 10 cc. alcohol were put into a small flask with a condenser and hydrogen conducted in continuously at 70 degrees. In a similar manner the activation of platinum was found to be 6700 to 37,000, that of iridium 2000 to 4000, silver and osmium very small, while gold and copper are not affected by hydrogen.

The Reduction of Unsaturated Organic Compounds. — The addition of hydrogen to unsaturated compounds with the aid of the platinum

* L. Mond, W. Ramsay und J. Shields: Zeit. f. anorg. Chemie, **16**, 325–328 (1898). See also Zeit. f. phys. Chemie, **26**, 109–112 (1898).

† C. Paal und C. Amberger: Ber., **38**, 1406–1409, 2414 (1905); **40**, 2201–2208 (1907).

‡ C. Paal und J. Gerum: Ber., **40**, 2209–2220 (1907); **41**, 2273–2282 (1908).

§ C. Paal und K. Roth: Ber., **41**, 2283–2291 (1908).

metals has been known for a long time. Up to the time of Paal, however, the metals had not been used for this purpose in colloidal form, but usually as platinum black. The reduction with the help of Co and Ni as catalytic agents according to Sebatier and Senderens, also Leprince and Siveke,* does not belong here. Debus † and Fokin,‡ and also Willstätter,§ recognized the principles of the reaction, and used it in the determination of constitution. Paal showed that other reductions of unsaturated compounds, such as acids, aldehydes, ketones, diketones, nitriles, etc., could be carried out even more satisfactorily than that of nitrobenzol.

The distinct advantage of colloidal metals over the powder form is doubtless due to the increase of surface and to the fact that the particles of metal and the molecules to be reduced are in more intimate contact. Both of these circumstances should aid the catalytic action.

The reduction of maleic and fumaric acids will be discussed as examples. The pure acid in alcoholic solution is not reduced by hydrogen. On the other hand the reaction is almost complete if the acids are neutralized with sodium carbonate and hydrogen introduced in the presence of colloidal palladium. The progress may be followed easily in a glass buret that is attached to an apparatus for shaking the reacting mixture, such as may be seen in Fig. 20. The mixture is brought into the vessel A, which is kept in motion by a shaking apparatus. C is a capillary tube and B is a gas buret. The air is first driven off by hydrogen and the entire apparatus saturated with it by means of shaking. Palladium must be in the vessel A while the shaking is going on. The substance to be reduced is now brought into the vessel A, care being taken not to introduce any air. The shaking is continued until there is no longer a rise of liquid in B. The difference in the two readings on the buret gives the number of

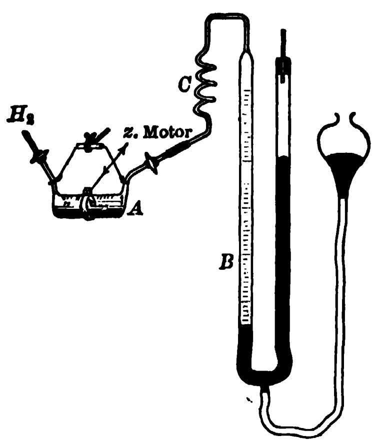


FIG. 20. Apparatus for Reduction with Colloids according to Paal.

* Leprince u. Siveke: D. R. P. 141029 (1902); C. (1903), 1, 1199.

† H. Debus: Liebigs Annalen, **128**, 200 ff.(1863).

‡ S. Fokin: C., 11, 758 (1906); II, 1324 (1907). Journ. russ. phys.-chem. Ges., **38**, 419 ff.; 39, 607 ff.

§ R. Willstätter und E. W. Mayer: Ber., **41**, 1475, 2199 (1908). Derselbe und E. Hauenstein: *Ibid.*, **42**, 1850 (1909). Derselbe und E. Waser: *Ibid.*, **43**, 1176 (1910); **44**, 3423 (1911).

cubic centimeters used in the reduction. Vessel *A* has a capacity of about 150 cc. The following proportions are suitable for the experiment: 0.1 g. fumaric acid dissolved in 10 cc. water, neutralized with sodium carbonate, and 0.08 g. of solid palladium colloid dissolved in 10 cc. water. Many organic substances may be reduced by this means.

Colloidal Copper

Colloidal copper is interesting because of its relation to copper ruby glass.* The constitution of this glass has been long under dispute. Some authors have held that the copper is in the form of cuprous oxide, while others believe the free metal is present. The deciding of this point is scarcely possible by analysis, but light has been thrown on it since colloidal copper has been made having the same color as copper ruby glass. Lottermoser † and Billitzer ‡ obtained brown, Gutbier § blue hydrosols by the reduction of copper salts or by electrical colloidation. Paal and Leuze ¶ have prepared both red and blue hydrosols by the reduction of colloidal copper oxide with hydrogen or hydrazine hydrate. The necessary copper oxide was made from copper sulfate to which potassium hydroxide and the sodium salt of lys- or protalbinnic acid had been added. The resulting dark blue liquid was dialyzed and evaporated. The reduction of copper oxide in a wet way by means of hydrazine takes place in two stages. At first an orange colored milky liquid is obtained that doubtless contains cuprous oxide. On further reduction the liquid becomes clear and is colored deep red. Paal and Leuze obtained liquids in this manner that were quite black in reflected but deep red in transmitted light. This agrees perfectly with the color of copper ruby glass. The author was able to convince himself with an apparatus of his own make that the red liquid gives the absorption lines near line *D* that are characteristic of copper ruby glass. The absorption lines were somewhat wider and the maximum displaced slightly toward line *C*, which would indicate that a partial coagulation had set in whereby flocculent complexes were formed, similar to the case of gold gelatin solutions on evaporation. Copper hydrosols should be investigated further with the ultramicroscope and also from the standpoint of spectral analysis.

Red copper hydrosol behaves differently, depending upon whether it is made with the sodium salt of prot- or lysalbinnic acid. The first

* R. Zsigmondy: Zur Erkenntnis der Kolloide, Chapter XVI (1905).

† A. Lottermoser: Journ. f. prakt. Chemie (2), **59**, 489–493 (1899).

‡ J. Billitzer: Ber., **35**, 1929–1935 (1902).

§ A. Gutbier: Zeit. f. anorg. Chemie, **32**, 355 (1902).

¶ C. Paal und W. Leuze: Ber., **39**, 1545–1549, 1550–1557 (1906).

gives an olive green color with sodium chloride, a phenomenon that has been observed in the case of copper ruby glass. The second becomes blue when treated in a similar manner. To sum up, the color of copper hydrosols may be red, brown, green, or blue.

Other Metal Colloids

Among other colloidal metals tungsten deserves mention because of its importance in electric light bulbs. A method for making the material for these filaments has been worked out by Kuzel.* The colloidal metal is obtained by continued grinding and by alternate treatments with acid and alkali. By this process the particles become so small that the metal finally forms a hydrosol. On precipitation of the sol a plastic mass is obtained that is next pressed out through fine holes, by which process threads are formed. The lamps are economical and last longer than the old varieties. Molybdenum, silicon, titanium, and thorium may be prepared in a colloidal state by the same method.

Wedekind † has demonstrated that zirconium sol may be made by etching the metal with hydrochloric acid. A powder is thus obtained that goes into colloidal solution on washing with water. This hydrosol gives very peculiar reactions with electrolytes. Most acids precipitate it, but tartaric and picric acids will not. The hydroxides of the alkali metals precipitate it immediately, but ammonia water does so very slowly. Most neutral electrolytes have little or no effect. It is probable that the treatment with HCl forms a protective colloid which causes the unusual behavior.

* A. Lottermoser: Chem.-Ztg., 311 (1908). Koll.-Zeit., **2**, 347 (1908).

† E. Wedekind: Koll.-Zeit., **2**, 289–293 (1908).

CHAPTER VI

COLLOIDAL NONMETALS

Colloidal Sulfur

SOBRERO and Selmi,* Wackenroder,† and Debus ‡ have studied the reactions between hydrogen sulfide and sulfurous acid, and have found that in addition to thionic acids colloidal sulfur is formed. Such hydrosols are generally turbid, and contain a portion of the sulfur in microscopic form,§ although most of it remains dissolved probably as amicrons. Raffo ¶ has recently devised a method for making perfectly clear colloidal sulfur solutions that have a considerable stability toward electrolytes. The procedure is as follows:

50 g. of crystallized sodium thiosulfate in 30 cc. of water are added drop by drop to 70 g. 1.84 sulfuric acid. The mixture is cooled and 30 cc. of water are added. The mixture is then warmed for 10 minutes at 80 degrees and filtered through glass wool. The precipitate is cooled, washed with water, warmed, and again filtered. This process is repeated a number of times. The purified sulfur mass is next centrifugalized and finally dissolved in water. The solution is neutralized with sodium carbonate, whereby most of the sulfur falls out. The liquid contains about 1 per cent sulfur and 6 per cent sodium sulfate. The precipitated sulfur dissolves completely in water, forming a clear liquid that contains 4.5 per cent sulfur and 1.5 per cent sodium sulfate. By dialysis the salt may be partially removed; however, continued purification will precipitate out the entire sulfur content.

The liquid mentioned above containing 1 per cent sulfur and 6 per cent sodium sulfate will give a precipitate on the addition of a half-normal solution of the potassium salt of sulphuric, nitric, or hydrochloric acid. The corresponding ammonium salts do not have this property. We have here to do with a very specific reaction toward electrolytes. While the colloidal solutions already discussed are pre-

* A. Sobrero et F. Selmi: Annales de Chim. et de Phys. (3), **28**, 210–214 (1850).

† Wackenroder: Archiv d. Pharmazie, **48**, 140, 272 (1846); Annalen d. Chemie u. Pharmazie, **60**, 189 (1846).

‡ H. Debus: Liebigs Annalen, **244**, 76–189 (1888).

§ J. Stingl und Th. Morawski: Journ. f. prakt. Chemie (2), **20**, 76–105 (1879).

¶ M. Raffo: Koll.-Zeit., **2**, 358–360 (1908).

cipitated by small amounts of electrolytes, these same small amounts are necessary to keep colloidal sulfur in solution. Larger concentrations on the other hand precipitate the sulfur. Sulfur solutions therefore resemble those of globulin, which are also not soluble in pure water, but require a small amount of electrolyte. Moreover, sulfur solutions resemble those of glue and soluble starch in that the sulfur

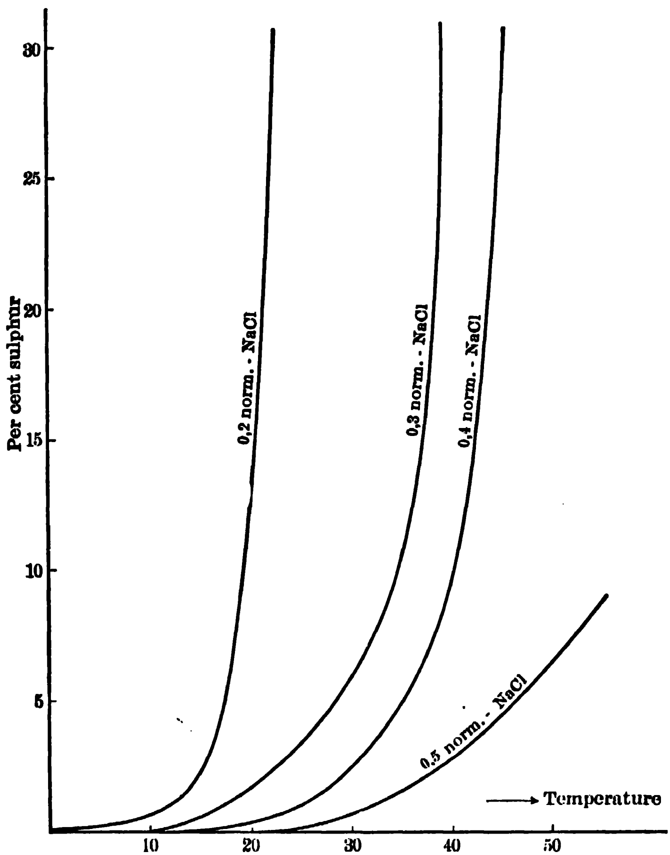


FIG. 21. Solubility of sulfur.

is more soluble in hot than in cold solution. On the contrary sulfur differs from glue and soluble starch in its behavior toward larger concentrations of electrolytes, as shown by the researches of Svedberg.*

The author has observed the peculiar behavior of sulphur hydrosols toward collodion membranes. The latter remove almost all of the sulfur from the liquid. Colloidal sulfur had a pressure against its

* The Svedberg: Koll.-Zeit., 2, 49–54 (1909).

filtrate represented by 136 mm. of water but sank toward the end of a month to 100 mm. At the end the inner liquid contained mostly amicrons.

As shown by Raffo sulfur comes out of colloidal solution and forms, on long standing, well-defined crystals having a normal melting point. These crystals dissolve easily in carbon disulfide but do not in water. In an endeavor to purify colloidal sulfur the author noticed that it lost its solubility. Just as long as it retains this solubility in water the colloid appears to be amorphous and somewhat plastic; it is also negatively charged. From this one must assume that the amicrons hold tenaciously to the impurities, water and electrolytes, and that these substances are responsible for the solubility in water. Svedberg has shown that precipitation with sodium chloride and decantation completely substitutes the chloride ion for the sulfate ion, but that the colloid still retains its solubility in water. The dependence of the solubility on the temperature and the concentration of the electrolyte is shown by the curves in Fig. 21. It is also quite remarkable that the colloidal sulfur obtained by Sobrero and Selmi was reversibly precipitated by sodium salts but irreversibly by the salts of potassium.

The presence of colloidal sulfur in the same solution with suspended sulfur was shown by Debus on evaporating the hydrosol. When about two-thirds of the water is evaporated the solution is clear and yellow. Dialysis separates out sulfur just as in the case of the preparation of Raffo. An elaborate investigation of the fractional precipitation of sulfur by Sven Odén * has shown that the larger particles are more easily precipitated than the finer ultramicrons.

Colloidal Selenium

In 1885, H. Schulze † prepared hydrosols of selenium by treating selenium dioxide with sulfurous acid. If sufficiently concentrated solutions are employed a precipitate is formed that will again dissolve in water. The hydrosols are fairly stable if kept in the dark, are clear, and appear red in transmitted light. On long standing the liquid becomes turbid and separates into two layers with a sharply defined boundary. The lower one contains most of the selenium and has a much higher specific gravity. By tipping the vessel the lower layer flows toward the lowest part of the bottom much as water does under an oil layer. However, it is still miscible with the upper layers and contains selenium particles that have not yet united but are separated from each other by water.

* Sven Odén: Zeit. f. phys. Chemie, **78**, 682–707 (1912).

† H. Schulze: Journ. f. prakt. Chemie (2), **32**, 390–407 (1885).

Colloidal selenium is sensitive to light. If a vessel is partially covered with black paper and allowed to stand in the light for a long time a lustrous precipitate of selenium is seen in the illuminated part of the liquid. Electrolytes precipitate colloidal selenium, while boiling causes the color to change to blue. When this blue liquid is shaken with carbon disulfide selenium separates out in the layer between the water and the carbon disulfide but does not appear to be dissolved. If the red liquid is shaken with carbon disulfide the selenium separates in the dividing layer but finally dissolves in the carbon disulfide. Especially beautiful red preparations that are rather stable toward electrolytes are obtained by the method of Paal.*

* C. Paal und C. Koch: Ber., **38**, 526–534 (1905).

CHAPTER VII

COLLOIDAL OXIDES

SCARCELY any other group manifests such varying properties and different reactions as do the colloidal oxides. They exist in all possible states of subdivision from the ionic to coarse suspensions. The hydrosols may be reversible or irreversible, stable or unstable, sensitive to electrolytes or not, and finally some are charged positively and some negatively. The properties of these colloids are to a much greater extent dependent upon the nature of the substance than are those of the metals, sulfides, or salts. In contradistinction to these properties that depend upon the substance is the relation between properties subject to gradual change because of concentration, previous history, or amount of peptising material present. This latter group of properties may vary over a wide range, and this makes the description of these colloids all the more difficult. We are met at the outset by an enormous number of facts, a comprehensive presentation of which would serve to confuse rather than to elucidate. This will be possible only after the systematic discussion of individual members.

In order to give an approximate idea of the varying relations we are confronted with here, the author has confined himself to a description of Graham's colloidal oxides, without making any attempt to be comprehensive. Such colloidal oxides have been chosen as are of general importance. For instance under colloidal silicic acid the formation of the most finely divided gels is discussed; under the hydrogel of iron oxide the investigations of Duclaux on conductivity and osmotic pressure are presented and remarked upon. Moreover in connection with this same colloid the important magneto-optical and ultramicroscopical researches of Cotton and Mouton on the construction of the ultramicron are taken up. Under colloidal stannic acid the relation of α to β forms, under the purple of Cassius the similarity of colloidal unions to chemical combinations, and under zirconium oxide the influence of the transition of dissolved crystalloidal substances to the colloidal state on the reactions and properties, are discussed.

The tendency of many colloidal oxides to appear in two modifications has been already referred to. We are not yet able to decide definitely whether we have here to deal with different substances in the chemical

sense, such as anhydrides, hydrates, polymers, etc., or whether it is a question of colloidal chemical properties resulting from differences in degree of dispersion. Many facts, however, point to the correctness of the latter view as will be shown in this and following chapters.

A. Colloidal Silicic Acid

The hydrogel of silicic acid appears in nature in the form of opal, hydrophane, and tabashir. The hydrogel, as is well known, is precipitated in a jelly form when most silicates are decomposed. By completely dehydrating the residue an insoluble powder remains.

Preparation and Properties of the Hydrosol. — The hydrogel may be prepared either by Graham's * method of dialyzing a mixture of water glass and hydrochloric acid, according to Grimaux † by the decomposition of the methyl ester of silicic acid with water, or by the effect of water on silicon chlorides or silicon sulfide.‡ Graham's method is as follows: 10 per cent sodium metasilicate and 10 per cent HCl are mixed together under constant shaking. In order to determine the correct relations for mixing, a trial experiment must be performed. Water glass is run into a definite amount of the acid until the solution begins to solidify, the shaking being continuous while the addition is being made. About two-thirds the amount of water glass necessary to cause solidification should be used to prepare the hydrogel. If it is found during dialysis that a jelly forms, the water glass employed should be diluted or the HCl used in more concentrated form. The hydrosol may be purified to a large extent by dialysis, and further concentrated if desired by evaporation.

A well purified and not too dilute hydrosol of silicic acid may be looked upon as an unstable system that has a constant tendency towards coagulation, and this coagulating tendency is more pronounced in the more concentrated solutions. It is seldom possible to increase the concentration to over 10 per cent. Graham once prepared a solution having 14 per cent colloidal silicic acid but it was so unstable that indifferent substances such as graphite or carbon dioxide served to coagulate it. Solutions under 1 per cent may be kept for years, and are fairly stable toward electrolytes. Some of the latter cause immediate precipitation, while others do so only after several hours.

Well-prepared silicic acid hydrosols are quite clear colorless liquids that scarcely exhibit any inhomogeneity under the ultramicroscope. If they are dialyzed with parchment membranes they frequently become

* Th. Graham: Liebigs Annalen, **121**, 36 (1862).

† E. Grimaux: Compt. rend., **98**, 1434–1437 (1884).

‡ E. Ebler und M. Fellner: Ber., **44**, 1915–1918 (1911).

turbid and contain submicrons. Jordis * considers it impossible to prepare colloidal solutions of silicic acid pure where the concentration is over 2 per cent. He attributes the stability of Graham's solutions to the presence of foreign substances, and even goes so far as to doubt the existence of SiO_2 as such in the solution. He thinks the alkali or acid forms compounds with the silicon dioxide. This assumption seems unnecessary to explain the stability of pure hydrosols. The relation may be similar to the case of supersaturated solutions where the stability depends upon the degree of supersaturation. Uncontrollable factors enter into the crystallization of supersaturated solutions, such as dust particles, and it is quite possible that conditions of one experimenter cannot be duplicated by another when working with hydrosols.

With regard to the purification of silicic acid hydrosols by dialysis, Zsigmondy and Heyer † have found that the chloride ion may be completely removed but that it is much more difficult to get the colloid free from sulfate. After long dialysis there remained 2 to 3 mols. of sodium sulfate for every mol. SiO_2. Such traces of electrolyte are almost impossible to get rid of. The hydrosol containing this quantity of sulfate could be concentrated by evaporation until the silicic acid is from 6 to 12 per cent of the entire mass. Well purified hydrosol depresses the freezing point very little, so that Sabanejeff ‡ obtained a molecular weight of 49,000 by this method. Bruni and Pappadà § could not observe any lowering of the freezing point with their preparations. The more sensitive direct measurement of the osmotic pressure shows that the colloid exhibits such against its filtrate. The pressure becomes smaller as coagulation proceeds.

Electric Charge. — The amicrons of the hydrosol are charged negatively and migrate toward the anode in neutral, alkaline, or weakly acid solution. During the electrolysis of neutral solutions silicic acid does not separate out at the anode as stannic acid and many other colloids do, but falls slowly to the bottom in striations much after the nature of sulfuric acid.

Precipitation with Electrolytes. — As already pointed out silicic acid is not immediately precipitated by all electrolytes. Hydrochloric acid, chlorides of the alkali, and alkaline earth metals give no precipitate but may cause gelatinization after standing for hours, days, or perhaps weeks. It is precipitated immediately by barium hydroxide,

* E. Jordis: Zeit. f. anorg. Chemie, **35**, 16–22 (1903).

† R. Zsigmondy und R. Heyer: Zeit. f. anorg. Chemie, **68**, 169–187 (1910).

‡ A. Sabanejeff: Journ. d. russ. phys.-chem. Ges., **21**, 515–525 (1889); Ber., **23**, R., 87 (1890).

§ G. Bruni e N. Pappadà: Atti della R. Accad. dei Lincei Roma (5), **9**, 354–358 (1900); Gazzetta chimica ital., **31**, **1**, 244–252 (1901).

concentrated solutions of ammonium sulfate, dilute solutions of egg albumin, glue, and many basic dyestuffs such as Methylene Blue. Regarding the effect of the salts of the alkali metals on the precipitation, Pappadà * found that the anions played little part but that the influence of the cathions increased with the molecular weight, cæsium having the greatest and lithium the least.

Protective Influence of Silicic Acid. — Silicic acid hydrosol does not act as a protective colloid for colloidal gold. It does not hinder the change of color by sodium chloride, neither does it prevent the formation of a turbidity nor a precipitate in silver chloride solutions, unless the amount of chloride ion is extremely small. In the latter case the reaction is obscure, and is not protective action in the ordinary sense. This is shown clearly by the addition of small quantities of suitable electrolytes such as sulphuric acid or potassium sulfate, when a turbidity is formed and precipitation occurs. The presence of two drops of concentrated sulfuric acid in 10 cc. of the hydrosol enables mere traces of chloride to be detected with silver nitrate almost as well as in pure water. Silicic acid hydrosols also prevent the formation of large particles of the noble metals. Indeed clear metal hydrosols may be obtained by this method. Real protective action occurs for the first time at the moment that the silicic acid is being precipitated. Under these conditions the change of color of gold solutions may be prevented and therefore the formation of large particles.†

Transitions of Silicic Acid. — Mylius and Groschuff ‡ have demonstrated that silicic acid at the moment of its formation from water glass is in the crystalloidal state and gradually goes into the colloidal state later. The newly formed silicic acid causes an appreciable lowering of the freezing point that gradually decreases as the formation of the colloid proceeds. The transition may be followed by means of reagents. For instance egg albumin causes no precipitation in freshly prepared solutions, but does so after the same solutions have stood for some time. In close connection with this is the loss of silicic acid during dialysis. Zsigmondy and Heyer § found that in the star dialyzer more than 90 per cent of the silicic acid went through thin collodion membranes which were sufficiently thick to prevent completely the passage of colloidal silver.

Crystallization of Silicic Acid. — Several authors have succeeded in obtaining crystals at higher temperatures from both the gel and the

* N. Pappadà: Gazzetta chimica ital., **33,** 272–276 (1903); **35,** 78–86 (1905).
† F. Küspert: Ber., **35,** 2815 (1902).
‡ F. Mylius und E. Groschuff: Ber., **39,** 116–125 (1906).
§ Zsigmondy und Heyer: l. c. page 135.

hydrogel of silicic acid. They were mostly quartz and tridymite. Senarmont * obtained quartz crystals by heating gelatinous silicic acid containing traces of hydrochloric acid for several days at 350 degrees. Chrustschoff † obtained quartz and tridymite by heating a dialyzed solution of silicic acid at 250 degrees for six months. Bruhns ‡ obtained quartz and tridymite by heating for 10 hours at 300 degrees after ammonium fluoride had been added to the dialyzed hydrosol. Although these crystals have been made at higher temperatures it is scarcely to be doubted that they may be formed, if very slowly, at the temperature of the room. Indeed a number of changes that occur when the hydrogel is kept for a long time in an atmosphere saturated with water vapor, may be best explained on the assumption of the formation of ultramicroscopic crystals from the ultramicrons.

Silicic Acid Gel

The gel of silicic acid originates from the hydrosol by coagulation either spontaneously or with the aid of electrolytes. Its properties are quite different from those of the precipitates of metal hydrosols. The latter are powders, and the particles are separated from the water. On the other hand the silicic acid hydrogel always contains water that cannot be completely removed by filtering or pressure. As is well known the water may be driven off by heating but the gel suffers an irreversible change. The same thing holds for the gel of other oxides. The water is more firmly held than by the gels of the colloidal metals.

This has been explained on the grounds that we are dealing with hydrates and not with oxides. For the general behavior of the gels it seems indifferent whether the nucleus is a hydrate or not. In a freshly prepared gel there are about 300 mols. of water to one mol. of silicon dioxide, and only about two-thirds of this water may be removed by rubbing and by filtration. Some gels rich in water possess elasticity which tends to prevent division. They may be rubbed into clumps that form larger lumps when a portion of the water flows off. The running together of the smaller lumps recalls the behavior of viscous liquids, and the comparison of gel formation to the separation of two liquids by Bütschli, van Bemmelen, and Quincke is thus far justified. However the assumption that the ultramicrons of gels or sols of lyophile colloids are themselves liquid, is no more reasonable than to insist that the molecules of liquids are liquid, or that the molecules of gases are gas. Any conclusion with regard to the particles themselves

* M. de Senarmont: Annales de Chim. et de Phys. (3), **32**, 129–175 (1851).

† K. v. Chrustschoff: N. Jahrb. f. Min. usw., 1, 205 (1887).

‡ W. Bruhns: N. Jahrb. f. Min. usw., **2**, 62–65 (1889).

that is based on aggregates is unjustifiable. The question of the state of aggregation of the ultramicrons remains undecided.

Because of the applicability of Boltzmann's * gas theory, which considers molecules to be completely elastic material particles incapable of much deformation, and because according to van der Waals † the properties of molecules must be compared with those of solids, it seems necessary to assume that the larger ultramicrons of a solid are themselves solid. The so-called liquid properties of gels rich in water would therefore be explained by the assumption that the ultramicrons are surrounded by water layers and have a certain free path and motion. This would make possible the surface tension effects that according to Quincke ‡ arise from the attraction of the electrically neutral particles for one another.

The water that is pressed out from the gel contains only a small portion of the colloid while the so-called viscous or oily liquid contains the remainder. These two "liquids" will be discussed later.

The Solidification of the Gel of Silicic Acid on Evaporation. — The dryer the gel becomes the more difficult it is to press out water. Table§ 22 gives an idea of the changes that the gel undergoes during dehydration.

TABLE 22

Number of mols. water to one mol. SiO_2.	Properties of the hydrogel.
40–30	Gel may be cut
20	Fairly stiff
10	Brittle
6	May be pulverized, powder apparently dry

The Change in Turbidity and in Volume During Dehydration.¶— When more water is driven off the volume decreases to a characteristic point, called by van Bemmelen the transition point, and designated by 0. From this on the volume remains constant. Further dehydration causes changes in the optical properties. The previously clear gel becomes turbid and chalk white (transition). The residue becomes clear again when the water content goes below 1 mol. The change in

* L. Boltzmann: Vorlesungen über Gastheorie, 34. Leipzig (1896).

† J. D. van der Waals: Die Kontinuität des gasförmigen und flüssigen Zustandes, page 34. Leipzig (1899).

‡ G. Quincke: Drudes Annalen d. Phys. (4), **9**, 793–836, 969–1045 (1902); **10**, 478–521, 673–703 (1903).

§ J. M. van Bemmelen: Zeit. f. anorg. Chemie, **59**, 225–247 (1908).

¶ J. M. van Bemmelen: Zeit. f. anorg. Chemie, **18**, 98–146 (1898).

volume can be seen in Table 23.* The addition of water causes little change of volume.

TABLE 23

Water content in mols.	Volume.
122	29
75.7	18
45.2	11
23.2	4
11.3	3
2.8	1
2.2	0.86
1.7	0.75
Transition	
1.0	0.73
0.39	0.73
0.3	0.73

Organogels of Silicic Acid

Important for their qualitative determination is the remarkable property of hydrosols that allows the water to be replaced by alcohol, acetic acid, glycerin, concentrated sulfuric acid, etc., and these liquids again by water without any appreciable change in the elasticity or transparency. Graham † was able to replace the water with alcohol, and thus change the hydrogel into a weakly opalescent alcogel having a volume almost identical with that of the hydrogel. The composition of the alcogel was as follows:

	Per cent
Alcohol	88.13
Water	0.23
SiO_2	11.04

By putting the alcogel into water the alcohol was replaced by the water without any marked change taking place in the properties of the gel. The same thing holds for sulfuric acid, nitric acid, formic acid, etc. Van Bemmelen obtained an acetogel containing,

1 mol. SiO_2
0.25 mol. H_2O
21.7 mols. acetic acid.

The fact that the water may be replaced by other substances as solvents without any marked change in the character of the gel, points

* J. M. van Bemmelen: Zeit. f. anorg. Chemie, **59**, 225–247 (1908).
† Th. Graham: Poggendorffs Annalen, 123, 529 (1864).

clearly, as van Bemmelen has noted, to the assumption that the water is not there as hydrate chemically combined, but is adsorbed water that fills the spaces between the ultramicrons.*

The Structure of Silicic Acid Gels as Revealed by the Microscope and Ultramicroscope. — The structure under the ultramicroscope of silicic acid gels is more pronounced † than that of gelatin of the same concentration. Silicic acid gels having a concentration of 1 to 3 per cent are most suitable although gels of higher concentration still exhibit discontinuity. These latter are very similar to gels of gelatin having a concentration of 1 to 2 per cent. The structure of these is more granular than that of more dilute silicic acid gels. The granular appearance is due doubtless to the joining of the ultramicrons together.

As in the case of gelatin, in very dilute solutions where the concentration of the colloidal silicic acid is about one-half of one per cent, flocculent precipitates are formed which contain large spaces filled with water. The constituents of the gel are no longer able to form a mass in which the ultramicrons are uniformly distributed. As the water content becomes less and less the spaces filled with water shrink, the particles of the colloid draw closer together, and it is thus clear why the gels from concentrated solutions exhibit a denser structure than those from more dilute solutions. That this is true to fact is shown by observations under the ultramicroscope during the formation of a gel,* and also from the polarization effects.

The Structure of Dehydrated Gels. — Bütschli ‡ has observed a honeycomb structure in many dried gels of silicic acid. The structure is not apparent until the spaces are filled with a suitable liquid such as chloroform or the oil of cedar. As soon as a portion of the liquid is evaporated the structure becomes discernible. Bütschli explains this on the assumption that the walls are too thin to be seen until the liquid has caused them to distend somewhat. If the liquid is partially evaporated off the thickened walls become visible. When the spaces are again filled with liquid the walls disappear because they are surrounded by a homogeneous medium. Bütschli has determined the interstices to have a diameter of 1 to 1.5 μ and the thickened walls 0.2 to 0.3 μ, and therefore the walls before they are treated with the liquid must be much finer than this. The work and measurements of Bütschli have been accepted by many investigators. To the author, however,

* G. Tschermak: Zeit. f. phys. Chemie, **53**, 349–367 (1905). G. Tammann: Zeit. f. anorg. Chemie, **71**, 375 (1911).

† W. Bachmann: Inaug.-Diss. Göttingen (1911). Zeit. f. anorg. Chem., **73**, 125–172 (1911).

‡ O. Bütschli: Untersuchungen über die Mikrostruktur künstlicher und natürlicher Kieselsäuregallerten. Heidelberg (1900).

it appears difficult to conceive that spaces filled with air, and having a diameter of 1 to 1.5 μ, can exist in a clear gel, as these spaces are enormous compared with the ultramicrons themselves. For, if the index of refraction of the disperse phase and the disperse medium differ at all, disperse systems having particles 1 to 1.5 μ are always very turbid even when the concentration is low. Such is the case of kaolin suspensions, clay suspensions, and oil emulsions. A much greater subdivision is necessary in order to have a clear colloidal solution. A SiO_2 foam filled with air where the spaces have dimensions of 1 μ and over must appear white and opaque because of the refraction and reflection of light, and manifest heterogeneity under the ultramicroscope. The observations reveal, however, that the dried gels often contain submicrons and often are quite empty from an optical standpoint. This points strongly to a much finer structure than Bütschli has ascribed to them.

The following experiment was carried out by the author. A clear dry gel having very faintly discernible submicrons was treated with the vapors of benzol, whereby it adsorbed 37 per cent of its own weight of the latter and remained optically clear. Under the ultramicroscope the benzol was allowed to evaporate, and the following process was seen to take place. First a faint light cone appeared that gradually became more pronounced. Then submicrons appeared that became so bright that they illuminated the neighboring particles. These submicrons could not be counted. Finally the light cone gradually became weak again. The submicrons were very thickly distributed and were quite like those in ruby glass. There were also particles just within the resolving power of the ultramicroscope.* Here, as in the case of ruby glass, heterogeneity could be observed, and forms composed of numerous amicrons piled up could be discerned. The light was linear polarized and the ray could be cut off by turning the nicol. This is another evidence for the fine state of subdivision.

The Transition. — The phenomena of the transition may be explained on the following grounds. The mixture of air and silicic acid is optically clear because both the particles and the spaces between them are amicroscopic. Only a few of the thicker masses of amicrons affect the light as submicrons, and can therefore be seen in the dried preparation. The coefficient of refraction of the amicroscopic mixture of benzol and silicic acid lies between that of benzol and that of silicic acid. Likewise the coefficient of refraction of the mixture air and silicic acid lies between that of the two substances. During the evaporation of the benzol countless tiny spaces are formed, filled with benzol vapor

* H. Siedentopf und R. Zsigmondy: Drudes Annalen d. Phys. (4), **10**, 1–39 (1903).

or with a mixture of air and benzol vapor. The spaces gradually become larger and we have a gas-silicic acid mixture with a coefficient differing from that of the benzol-silicic acid mixture.* Light is now refracted and when the gas filled spaces become large enough submicrons may be detected. Fig. 22 represents a schematic view of the process.

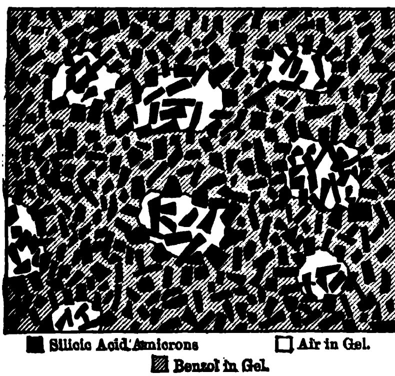


FIG. 22. Submicroscopical air bubbles in the gel of silicic acid.

The gas filled spaces in the silicic acid skeleton grow in an irregular manner, and when they become large enough the structure appears honeycombed. According to this point of view the walls surrounding the spaces consist of silicic acid soaked in benzol, and the spaces of Bütschli as gas filled silicic acid. An observation by Bachmann † corroborates this idea. With a silicic acid gel soaked in benzol he saw, in the ultramicroscope during the evaporation, a constantly changing picture. Large numbers of submicrons appeared and disappeared again under the eye of the observer. Blocks of ultramicrons were formed and were continuously torn asunder. This is to be attributed to the withdrawal of the benzol and the changing distribution of liquid and gas in the amicroscopical canals. With complete evaporation of the benzol the system loses its coarser heterogeneity and the original weak dispersion of the light is again established, which does not correspond to the finest structure of the gel.

From what has been said it may be concluded that Bütschli's honeycomb is not the true structure of the gel, but on the contrary is a coarser heterogeneity due to the accumulations of liquid in a silicic acid conglomerate, which is permeated with amicroscopical spaces.

Dehydration of Silicic Acid by Periodic Reduction of Pressure

Van Bemmelen ‡ has carried out elaborate and important experiments with regard to the behavior of silicic acid hydrogels during dehydration. He put the hydrogel into desiccators, 36 in number, con-

* D. Brewster: Philos. Transact., **11**, 283 (1819). Schweiggers Journ. f. Chem. u. Phys., **29**, 411–429 (1820).

† W. Bachmann: Zeit. f. anorg. Chemie, **73**, 165 (1911).

‡ van Bemmelen: Zeit. f. anorg. Chemie, **13**, 233–356 (1897); **59**, 225–247 (1908); **62**, 1–23 (1909). J. S. Anderson: Zeit. phys. Chemie, **88**, 191–228.

taining varying concentrations of sulfuric acid, and in this manner graded the aqueous vapor pressure from 0 to 12.7 mm. The hydrogel was first put over the most dilute sulfuric acid and left until the weight ceased to shrink. This was continued down the row of desiccators until the last contained the most concentrated sulfuric acid. The results showed that the dehydration was not the same for all gels, but depended upon the method of preparation and the previous history. The process is shown schematically in Fig. 23.

The vapor pressure decreases along the curve A_β while the volume simultaneously decreases. In point O, the transition point, the curve breaks suddenly. Along the line OO_1 water is given up by the gel at almost constant pressure. The volume of the hydrogel remains almost

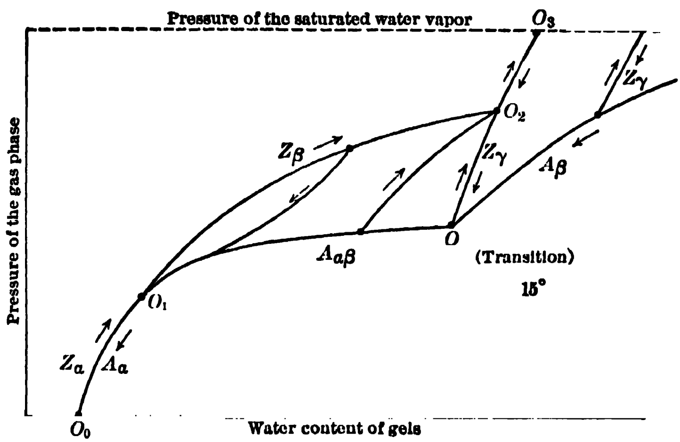


FIG. 23. Water content of the gel.

constant in spite of the loss of water. Along the line OO_1 a peculiar phenomenon takes place; the previously clear gel becomes turbid, clears up again, and at O_1 is completely clear. Further dehydration follows the line A_α; the last stages are possible only by the employment of red heat. It is remarkable that the dehydration along the curve A_β is quite irreversible, and if water is now added a new curve is followed, *viz.*, curve Z_γ. On the contrary the curve OO_1 represents a completely reversible process at every point. Curve $Z_\alpha Z_\beta$ is the hydration process, probably an example of hysteresis. If the gel is again dehydrated curve Z_γ is followed.

From the fact that the point O represents two mols. of water to one mol. of silicic acid, and that point O_1 represents one to one, it may be concluded that the process is one of decomposition of a hydrate. The vapor pressure at O is the vapor pressure of the orthohydrate and the

turbidity is caused by the appearance of a new phase. This point of view is contradicted, however, by several curves of van Bemmelen. He found that the points O and O_1 did not correspond in the majority of cases to 2 mols. and 1 mol. of water respectively, but that the former might lie between 1.5 and 3, while the latter usually lay between 0.5 and 1. Van Bemmelen objected to the assumption of hydrates from the above considerations. To the author it seems much more reasonable to assume that the dehydration along the line OO_1 is to be attributed to the emptying of the spaces in the gel, because they may be filled by many other liquids such as alcohol, benzol, benzine, etc., and still the phenomenon of turbidity occurs during the evaporation of the liquid in question.

An important question in this connection is the size of the spaces concerning which considerable has already been said. From the evidence it seems probable that they must be very small. That they must be connected with one another is indicated by the rapidity with which a liquid will completely permeate the entire mass of the gel. If we assume that these spaces are tiny capillaries then the dehydration must obey the laws of capillarity, and from this some idea of the size of the capillaries may be obtained.

$$P_B - P_0 = \frac{g_B}{g_A - g_B} \cdot T_{AB}\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

Here P_0 is the saturation pressure over the level liquid.
P_B is the saturation pressure over the center of the meniscus.
T_{AB} is the surface tension.
g_A is the density of the liquid.
g_B is the density of the vapor.

According to the formula, a lowering of the vapor pressure of 6 mm. would correspond to a capillary diameter of 5 $\mu\mu$. A capillarity of this degree of fineness would agree with the optical properties of the hydrogel.

Application of the Theory of Capillarity to the Process of Dehydration

I. Let us now see if van Bemmelen's curves can be accounted for on the basis of the laws of capillarity. In order to understand this better it is perhaps necessary to recall some of the theory of capillarity.* Assume a liquid touching a capillary tube forms a meniscus concave upwards, as represented in Fig. 24. Because of the surface tension on the liquid it rises in the capillary. The pressure upward,

* B. E. Riecke: Lehrbüchern der Physik (3 Aufl.), 1. Leipzig (1905).

represented by $2\pi rT$, is equal to the weight of the liquid raised, $r^2\pi h\sigma$, where T is the surface tension, h is the height of the column of liquid, and σ is the specific gravity of the liquid.* From this it follows that

$$h = \frac{2T}{r\sigma}.$$

The formula holds only for a liquid completely surrounded by very small cylindrical capillaries. Then the radius of the curvature of the liquid gas surface is equal to the radius of the tube. The theoretical height of water in capillary tubes having a diameter of 5 $\mu\mu$ would be several kilometers. If the radius of curvature is very small and the height correspondingly great the liquid would evaporate under a pressure considerably less than that which it would have from a plane surface. The lowering of the vapor pressure may be calculated from the formula given on page 144.†

II. If the liquid is not completely surrounded the angle that the liquid makes with the solid varies from O upwards, and the radius of curvature would be greater than the radius of the tube. Consequently the height must be less and the vapor pressure greater. This is of importance in connection with hydration curves.

III. Wherever the meniscus is concave toward the gas, surface tension exerts a pull on the liquid. The result of this pull is the rise of the liquid in the capillary. A corresponding and opposite pressure is exerted on the capillary. Where the capillary is vertical this pressure is equal to the weight of the liquid raised.

What has been said will be sufficient to make the dehydration curves or isotherms clear. Let us consider gel in the curves $OO_1\,O_0\,O_2\,O$. We may imagine the gel in point O to contain numberless tiny capillaries filled with liquid. The surface of the liquid in each capillary is a half sphere with the concave surface toward the gas, and a very small radius of curvature because of the miniature dimensions of the capillaries. According to (1) such an arrangement causes an enormous pull on the liquid in the direction of the upright arrows in Fig. 24 and a corresponding pressure in the opposite direction on the walls. The latter would press the amicrons in the walls close together and cause a contraction of the gel, while the former would favor the escape of tiny air bubbles from the interior of the gel. These bubbles would therefore cause the turbidity in the transition point.

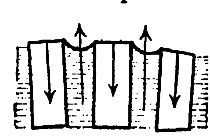


FIG. 24.

* B. E. Riecke: Lehrbüchern der Physik (3 Aufl.), 1. Leipzig (1905).

† Lord Kelvin: Proc. Roy. Soc., 7, 63–68 (1870).

(5) The state of the gel in O is characterized by a dilatation of the enclosed liquid and a compression of the surrounding silicic acid.

Both the compression of the silicic acid and the dilatation of the liquid are dependent upon the radius of curvature of the liquid surface, Fig. 25. Both are large when R is small, and both approach zero when R is approaching infinity, that is when the surface of the liquid is a plane. On the addition of a very small amount of water the radius of curvature would be greatly increased, and the surface tension relations in the gel would be changed a great deal. In other words there would be a decrease in the surface tension, in the compression of the silicic acid, and in the dilatation of the liquid. The liquid would therefore contract, the gel would expand somewhat, and take up a corresponding amount of water. These relations are of importance in the consideration of the curves Z_γ and the addition of water from O_2 to O_3.

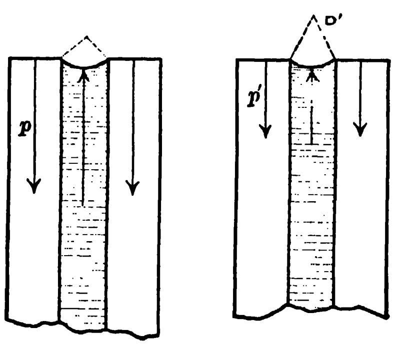


FIG. 25. $R < R'$ and $p > p'$.

Dehydration of the Hydrogel

The fact that the water can be evaporated at normal vapor tension until the relations are about 6 mols. water to 1 mol. silicic acid would indicate that this water is loosely joined, or can be easily pressed out. From the reduction of the vapor tension for quantities less than 6 to 1 it may be concluded that the meniscus begins to be concave toward the gas phase at this point. From the reduction of the vapor tension along curve A_β we cannot calculate the diameter of the capillaries because the volume of the gel varies continuously until O is reached. The formula given above is not applicable until the gel ceases to contract by further dehydration. These conditions obtain at the transition point so that the formula may be used to calculate the size of the capillaries.

Dehydration Along the Line OO_1. — Bütschli has observed, and it has been corroborated by work with the ultramicroscope, that the dehydration does not go on from the outside toward the interior, but that holes are formed in the interior free of liquid. It may be assumed that at point O the water on the surface capillaries has a radius of curvature corresponding to the vapor tension, as shown in Fig. 26. According to 3, page 145, this would cause the evolution of gas in the interior of the mass much like the effervescence under reduced pressure of a

liquid saturated with gas. The horizontal position of the curve OO_1 would indicate that the radius of curvature of the capillaries in the interior is very little greater than those on the surface. In point O_1 the capillaries are almost empty and the curve O_1O_0 represents the withdrawal of the adsorbed water, or possibly water of hydration.* In the latter case it would be necessary to assume, as Tammann † has done for the water contents of many crystallized minerals, that the hydrate and the anhydride formed a solid solution. As already intimated, the dehydration along this curve is quite reversible and the equilibria are quickly established.‡

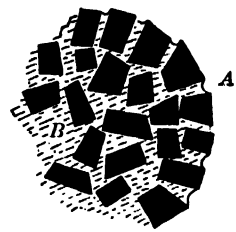


FIG. 26. *A*, Surface of gel. *B*, Interior.

The Addition of Water to the Gel. Filling the Capillaries. — The variation of the curve O_1O_2 from O_1O may be explained on the following grounds. It is well known that a liquid will not rise to the same height in single tubes as it will if the tubes form a network. In other words the radius of curvature is greater in the single tubes. But a greater radius of curvature corresponds to higher vapor tension. From this point of view the filling of the tubes occurs under a greater vapor tension than did the dehydration, because all the tubes are filled with liquid in the latter case as long as the water suffices. This seems to be the simplest explanation of the hysteresis in the field OO_1O_2O. The water does not cover all the tubes at first; the radius of curvature is greater, and therefore the vapor tension is greater during the addition of water than during the dehydration. The air in the mass doubtless prevents the water from completely filling the network of tubes. Other explanations of the hysteresis are possible.§

In point O_2 the capillaries are again filled, but the vapor tension is greater than it is at the transition point. So also is the radius of curvature and this corresponds to a lessened pressure on the gel. As a consequence the gel can take up more water than it can at O and the point O_2 therefore lies somewhat to the right of O.

The position of the y-curves may be explained on the same grounds, *viz.*, the change in the radius of curvature. The gel is not capable of distension except within the limits of elasticity. In point O_3 the vapor tension in the gel is equal to that of water at the same temperature, consequently the water in the gel must have a plane surface toward the

* H. Freundlich: Kapillarchemie, 491.

† G. Tammann: Zeit. f. phys. Chemie, **27**, 323–336 (1898).

‡ van Bemmelen: Zeit. f. anorg. Chemie, **13**, 258 (1897).

§ H. Freundlich: Kapillarchemie, 486 ff.

gas phase. Along the curve O_2O_3 there is, therefore, no pressure on the gel. This same explanation would hold for all other Z_γ curves and the almost straight line formation indicates the correctness of the underlying assumptions.

Irreversible Changes of State. — The dehydration of the hydrogel of silicic acid along the curve A_β presents two important questions.

1. Why is the reaction along the curve A_β not reversible?

2. What is the nature of the irreversible change of structure, along the curve A_β? As will be shown later van Bemmelen has demonstrated that a change in the position and in the length of the curve OO is brought about by ageing of the gel under constant vapor pressure. See Fig. 27.*

With regard to the first question there are several possibilities, and these require further careful study before comprehensive discussion is possible. The second seems to present more vulnerable points of

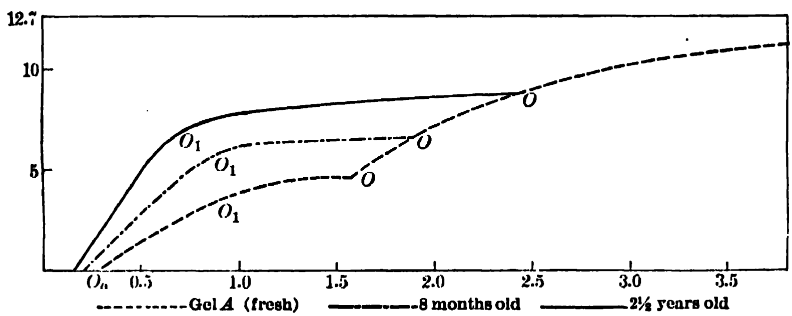


FIG. 27. Effect of ageing.

attack. In considering the change of structure with the lapse of time, two reactions that play an important part in all colloidal chemistry must not be lost sight of, *viz.*, the union of the particles, and the growth of the larger particles at the expense of the smaller, possibly also the growth by crystallization. Both must lead to an enlargement of the interstices between the particles and to a solidification of the gel residue, by which the total volume of the gel remains almost constant, under constant vapor tension.

Influence of Ageing. — If crystallization or other processes that enlarge the spaces between the particles, occur during the ageing of the gel, the vapor tension of such aged gels must be higher than that of the newly prepared. This can be seen from Fig. 27. The older the gel, the higher is the vapor pressure at the transition point. The ageing of the particular gel investigated took place at the saturation point of aqueous vapor.

* van Bemmelen: Zeit. f. anorg. Chemie, **13**, 345 (1897).

The Volume of Air in the Spaces Between the Particles

Van Bemmelen * found the following specific gravities for dried gels.

A (fresh), No. 107	1.17
A, 6 months old, No. 105	1.05
A, 5 years old, No. 106	0.9

From this and from the specific gravity of the gel substance itself, he calculated the volume of the spaces, evaluated against 1 volume of the gel substance.

A (fresh)	0.71
A, 6 months old	0.94
A, 5 years old	1.25

The volume of the adsorbed air is considerably greater than that of the spaces, from which it follows that the air must be condensed. 1 volume of the interspace contained the following volumes of air calculated at normal temperature and pressure.

A (fresh)	4.2
A, 6 months old	2.65
A, 5 years old	2.0

These figures indicate that a decrease in the total surface of the particles must occur during the ageing, because the smaller the surface exposed the less gas could be adsorbed. At the same time the interspaces are becoming larger, and this would go to show that the ultramicrons are growing at the expense of the smaller in a manner similar to a crystallization process.

Effect of Ignition

A low red heat for a short time left the gel in such a state that the dehydration curve was very similar to that of the unheated gel except that the interval of constant pressure OO_1 is very much shorter. Longer heating had the same effect as may be seen from Fig. 28, taken from the article by van Bemmelen.† Strong ignition robs the gel of its property of taking up water to any large extent.

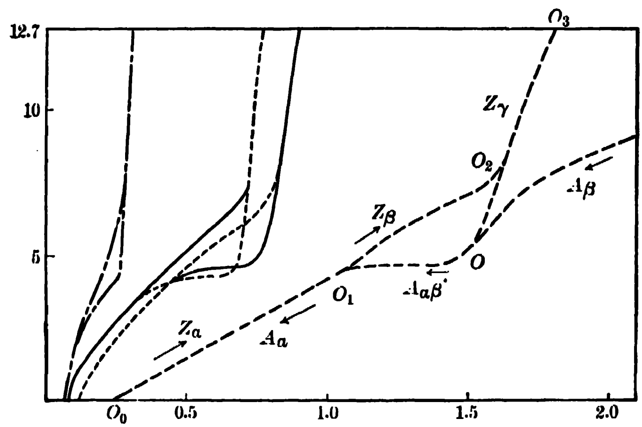
According to Bütschli ‡ the amount of salt in the gel (difficult to remove by washing) has an influence on the changes during heating. While salt-free gel did not change very much in the interior, those containing salts became turbid and lost their power of taking up water

* van Bemmelen: Zeit. f. anorg. Chemie, **18**, 114–117 (1898).

† *Ibid.*, **13**, 350.

‡ O. Bütschli: Untersuchungen über Mikrostruktur. usw., 337.

easily. A honeycomb structure could be detected in some of these heated gels. From the curves and from microscopical observations one may conclude that because of unequal heating in the crucible the particles melt together in the spots that are at the higher temperature, and that traces of salt are favorable to this reaction. On the other hand those spots that are not heated to the requisite temperature, or are free from salt, retain their original structure, and at the transition point must have the same vapor tension as they had before the heating. However as a portion of the original pores will be damaged on each heating the total amount of water that the gel will take up must be less than before the heating. This would account for the fact that the line OO_1 becomes shorter as the heating is continued.



------Gel A_1 Fresh Gel A_1 Short Heating———-------Gel A_1 Again Heated
——·——Gel A_1 Fresh after Dehydration. Heated strongly 10 Minutes

FIG. 28. Effect of red heat.

Staining the Gel of Silicic Acid

Corresponding to its large surface silicic acid gel has considerable power of adsorption, and this can be most easily demonstrated with dyestuffs. Acid dyestuffs are feebly adsorbed and may be almost completely removed by washing. Basic dyestuffs, on the contrary, are adsorbed to a large degree, and the reaction is practically irreversible; that is the dye cannot be removed by washing. To explain this it would be natural to suppose that the silicic acid formed a salt with the basic dye. Opposed to this point of view is the fact that charcoal and many other substances behave similarly toward acid and basic dyestuffs. For instance, Fuchsin, Methyl Violet, and Malachite Green are sometimes adsorbed to give intensive colors that cannot be removed by washing, while acid dyestuffs may be easily removed by this process.

Tschermak * has performed some experiments on the staining of gels obtained from the decomposition of various mineral silicates and found that the moist gel did not adsorb so well as the dry. He further demonstrated that silicic acid from different sources adsorbed in a varying manner, depending upon the origin and method of preparation. Kaolin, studied by Suida,† gave results in accord with gels from minerals. This is probably due to the fact that the surface of the kaolin particles is covered with silicic acid gel, because the reaction is not changed if kaolin is treated with hydrochloric acid. Again if the kaolin is etched with hydrofluoric acid so that the surface is no longer silicic acid but rather the oxides of the aluminium group, acid dyestuffs are adsorbed just as in the case of aluminium oxide. According to H. Ambronn ‡ silicic acid gel becomes brown in a violet solution of iodine, and Küster has made use of this reaction as a test for the presence of the gel in plants.

Reaction of the Dehydrated Gel Towards Hydrosols

As already pointed out the mass of a silicic acid gel is permeated with extraordinarily fine pores. This is consistent with its power of becoming wet through and through very quickly by water. It also explains why crystalloids pass easily through, and why it becomes colored by dyestuffs, but does not permit the passage of colloidal particles. The author has made use of this last property for the purposes of ultrafiltration.

If the gel is thrown into fuchsin solution the dye is soon adsorbed. In colloidal solution the dry gel soaks up the water like a sponge, leaving the colloid in a mass on the surface. A piece of the dry gel dipped into a 10 per cent solution of colloidal silver and immediately removed has a highly reflecting silver mirror on the surface. Benzopurpurin remains on the surface and does not penetrate any but the larger cracks. The same may be said of Carmine and colloidal iron oxide. Because the gel bursts into smaller pieces during these experiments it is wise to follow the reaction under the microscope, using a magnification of 20 to 30 diameters. The excess of the hydrosol may be removed by water or by alcohol.

A series of interesting reactions may be observed under these conditions. Generally the gel breaks up into smaller pieces in the first few moments. This is doubtless due to the pressure to which the air in the pores is subjected, and to changes of surface tension in the gel.

* G. Tschermak: Zeit. f. phys. Chemie, **53**, 349–367 (1905).

† W. Suida: Sitzungsber d. Akad. d. Wiss., Wien, **113**, IIb, 725–761 (1904).

‡ E. Küster: Ber. d. D. Botan. Ges., **15**, 136–138 (1897).

See the discussion on page 144, on capillarity. The water spreads into the interior rapidly at first, and more slowly toward the end. As this goes on more tiny explosions take place with the accompanying splitting of the gel, or air bubbles are formed at tiny cracks along the surface of the particles. Both the moistened and the dry gels are transparent, but differ in the coefficient of refraction. As a consequence the reaction is much more easily followed. The gel filled with air appears like an air bubble surrounded by a strongly refracting medium. As the bursting of the gel or the evolution of the air progresses the volume of the air spaces gradually diminishes and finally disappears. Benzine is even more suitable for the purpose because of its smaller surface tension and consequent slower penetration into the mass. There is here very little evidence of explosion so manifest in the case of water.

Occurrence of Silicic Acid in Nature

Silicic acid gel in a more or less hydrated form occurs in nature as opal, chalcedon, agate, hydrophane, etc., and in the vegetable kingdom as tabashir. Hydrophane and tabashir possess a great similarity to artificial gels. They also take up water with the evolution of gas (air) bubbles and are more or less transparent according to the water content. Sometimes however, they are chalk white. Change of the water content of opal causes the same splitting process that is so common with the artificial gels. Liesegang * has shown that agate has probably been produced from a gel of silicic acid into which layers of iron and other salts have penetrated. The process is probably similar to that on which his observations were made, *viz.*, the diffusion of silver nitrate in gelatin containing chromate.

B. Colloidal Stannic Acid

The Hydrosol of Stannic Acid

According to Graham † the hydrosol of stannic acid may be made by the addition of alkali to solutions of stannic chloride, and subsequent dialysis, or by the dialysis of sodium stannate after the addition of hydrochloric acid. The gels thus obtained may be peptised by further dialysis. Excesses of alkali may be neutralized by the addition of iodine solution. According to the same investigator colloidal stannic acid is changed on heating to metastannic acid. E. A. Schneider ‡

* R. E. Liesegang: Centralbl. f. Min. Geol. usw., 593–597 (1910); 497–507 (1911).

† Th. Graham: Poggendorffs Annalen, **123**, 538 (1864).

‡ E. A. Schneider: Zeit. f. anorg. Chemie, **5**, 82 (1894).

prepared the hydrosol in a similar manner except that he employed ammonium hydroxide instead of sodium or potassium.

The author has succeeded in preparing a hydrosol that is relatively free from electrolytes without the inconvenience of dialysis, by the following methods.* A current of air is conducted through a very dilute solution of stannous chloride until oxidation is complete. A precipitate separates out that may be freed from chloride by washing and decantation, and which is soluble in very little ammonium hydroxide. The excess of ammonia is easily evaporated on boiling. A still more simple method † is to dilute a solution of stannic chloride whereby the latter is hydyrolyzed almost to completion. This gel may be washed by decantation and peptised as in the above method. After the boiling both gels contain 1 mol. of ammonia to 20 to 30 mols. SnO_2.

The hydrosols are very stable, almost optically clear and may be kept for years without any change taking place in the appearance. That the appearance is deceptive, however, is shown by the fact that the protective effect on colloidal gold gradually lessens. On freezing leaf-like crystals are formed that are no longer soluble in water.

As in the case of all other hydrosols that of stannic acid exhibits certain exceptional reactions. Most electrolytes, such as sodium chloride, hydrochloric acid, potassium hydroxide, etc., precipitate it at once. Toward sodium chloride and many other alkali salts hydrosols of stannic acid differ in their behavior from those of silicic acid. The latter are not immediately coagulated but on the contrary fall out slowly. The precipitation with potassium hydroxide or sodium chloride is reversible; that is to say the precipitated stannic acid goes back into solution as soon as the electrolyte is removed by washing. On the other hand the coagulation with acids is irreversible, and the precipitating agent may be washed out completely without losing any of the gel. See the chapter on peptisation, page 74.

If the solution is boiled too long the colloidal stannic acid becomes an almost insoluble glassy mass that cannot be again peptised. The author noticed that an aged solution on long boiling gave a rubber-like viscous stringy mass that was soluble in water. Complete dehydration destroys the soluble properties of stannic acid gels to such a degree that they may not be peptised. On electrolysis the stannic acid is precipitated on the anode in the form of a transparent gel. The process is similar to the electrolysis of salts where the acid has a high molecular weight, and also to that of some dyestuffs.

* R. Zsigmondy: Liebigs Annalen, **301**, 369 (1898).

† *Ibid.*, 370.

Protective Effect of Colloidal Stannic Acid. — Contrary to the behavior of silicic acid the freshly prepared hydrosols of stannic acid have a protective effect on colloidal gold, sometimes even in the presence of sodium chloride. If dilute hydrochloric acid is used instead of sodium chloride, a deep red or purple red precipitate is obtained, which is known as the gold purple of Cassius.

α and β Stannic Acid

Two sorts of stannic acid are known in experimental, and also in analytical chemistry. They have been called α and β, or ordinary and metastannic acid. The first modification is prepared according to the well-known method of treating a solution of stannic chloride with a limited amount of alkali; the second is made from the first by different processes. The β form is the more stable because the α form always turns to the β, or to a product intermediate between α and β. The latter may be made directly by the action of nitric acid on tin. In the water content the two modifications do not differ materially, as shown in van Bemmelen's article.*

In a moist atmosphere the α form takes up more water than does the β. The differences of the chemical properties are treated in any standard work on analytical chemistry. It seems very probable that these reactions are between different colloidal modifications. If one attempts to get them in crystalloidal form, which can be done by treatment with concentrated alkalis or acids, identical solutions are obtained, *e.g.*, stannates or $SnCl_4$, etc. The hydrochloric acid solution, where the acid is not too concentrated, contains beside the stannic chloride a considerable amount of colloidal stannic acid, or colloidal oxychloride. The presence of this latter can be easily demonstrated by the addition of red gold solution. The protective action is so great that acids will not precipitate the gold. Stannic chloride solutions immediately after dilution contain a considerable quantity of colloid formed by hydrolysis; in fact enough to have a protective action.† Only concentrated solutions of stannic chloride precipitate the gold and cause the customary change of color. This is also true of the β form regardless of whether it has been made from α stannic acid by standing, or by peptisation of the body made from nitric acid and tin.

It is quite possible that the differences in the chemical reactions of the two modifications may be explained on colloidal grounds, without the assumption of isomers or polymers. The somewhat turbid appear-

* van Bemmelen: Ber., **13**, 1466–1469 (1880).

† P. Pfeiffer: Ber., **38**, 2466–2470 (1905); L. Wöhler: Koll.-Zeit. **7**, 243–249 (1910).

ance, and the lesser stability toward electrolytes of metastannic acid would indicate that the particles were larger than those of the α form. It is scarcely to be doubted that the large number of modifications described by Fremy, and Musculus are likewise colloidal varieties or mixtures of α and β forms. The author has already called attention to varieties having properties midway between the α and β forms, and has suggested the possible significance.*

The idea that β stannic acid is a colloidal modification was suggested by van Bemmelen and later more elaborately presented by Mecklenburg.† The latter is quite right in holding that there is no difficulty in explaining the fact that the two modifications under suitable conditions retain their specific properties after coagulation; that is, they may be again dissolved to reform α and β stannic acid. Doubtless the coagulation of a colloidal solution involves the union of the particles to form larger complexes, and these complexes are not homogeneous masses, but are masses of particles that retain their individuality.

As already pointed out β stannic acid contains larger particles because it adsorbs less water than the α form. Furthermore α stannic acid is obtained from crystalloidal solutions so that it is natural to suppose it contains smaller particles. Weber ‡ has shown that α stannic acid is formed at first from nitric acid and tin if the solution is sufficiently cooled. This solution is to be considered, according to Mecklenburg, as α stannic acid dissolved in nitric acid. On boiling the concentrated solution β stannic acid is formed, but according to Rose§ the α form may be separated out if the solution is sufficiently dilute. Another experimental fact, leading to the belief that the β form contains the larger particles, is the reversibility of α stannic acid in contradistinction to β. The latter is also much more difficult to return to the crystalloidal state.

Stannic Acid Gel

The gel of stannic acid may be obtained either by evaporating the hydrosol or by precipitation with electrolytes. By the first method a transparent jelly is obtained that becomes glassy on drying and resembles the gel of silicic acid. In the second case flocculent masses are the result of the precipitation.

Peptisation. — Only those rich in water may be easily peptised, not dried residues. In the theoretical part attention was called to a

* R. Zsigmondy: Liebigs Annalen, **301**, 361–387 (1898).

† W. Mecklenberg: Zeit. f. anorg. Chemie, **64**, 368–374 (1909). van Bemmelen: Recuil d. travaux chim. des Pays-Bas, **7**, 98 (1888).

‡ R. Weber: Poggendorffs Annalen, **122**, 358–371 (1864).

§ H. Rose: Journ. f. prakt. Chemie, **45**, 76–86 (1848).

condition of vital importance for peptisation, *viz.*, that the particles must be very fine. We can suppose now that the hydrogel contains the same particles in aggregate that existed in the hydrosol and that these particles have the same individuality in both conditions except that the electric charge is lacking in the gel, and the ultramicrons have therefore a greater cohesion for one another. When alkali is added the particles diffuse into the liquid as already described on page 75. By gradual dehydration the bonds between the particles become stronger and peptisation is thus rendered more difficult. Finally when the dehydration is complete the particles unite so that peptisation is now impossible. The gradual change of properties toward the irreversible as dehydration progresses, is a common result in colloidal chemistry. The simplest explanation for this phenomenon is that just offered.

Purple of Cassius

The purple of Cassius is that purple or brown precipitate that is obtained when a gold solution is treated with stannous chloride. The red coloration that precedes the precipitation is a well-known delicate test for gold. The precipitate is used extensively in china painting because of the beautiful red color. It was discovered by Andreas Cassius in Leyden in 1663 and because of its importance in ceramics has been made by various processes. Beside the method mentioned above the precipitate may be obtained by treating an alloy of gold, tin and silver with nitric acid. The stannous chloride procedure is as follows.*

200 cc. gold chloride solution, containing 3 g. gold as $HAuCl_4$ per liter, and 250 cc. of a solution of stannous chloride (3 g. tin as $SnCl_2$ per liter, and a very small excess of hydrochloric acid) are poured into 4 liters of water and violently shaken. On standing for about three days the dark violet red powder will have fallen to the bottom and the liquid should be clear and colorless. The latter contains neither gold nor tin. The precipitate should be washed by decantation until there is no test for chlorides, filtered by suction and again washed. It is next stirred up in water and a very little concentrated ammonia added, when the gold should dissolve to form a clear solution on boiling.

Richter, Gay-Lussac and others have contended that the purple is a mixture of gold and stannic acid. Several writers, among others Berzelius, have objected to this point of view. Berzelius was aware of the existence of mixtures of gold and stannic acid but noted that the latter were brick red and somewhat turbid. Further, these solutions could be treated with aqua regia whereby the gold and the stannic acid could be separated. Such is not so in the case of the purple of

* R. Zsigmondy: Liebigs Annalen, **301**, 365 (1898).

Cassius. The solubility in ammonia indicates a compound of a chemical nature, for according to Berzelius when the stannic acid dissolves in ammonia the gold should remain behind if the mass were only a mixture. He conceived the purple to be a chemical combination having the composition indicated by the formula:

$$Au_2O_2 \,.\, 2\, Sn_2O_5 \,.\, x\, H_2O.$$

According to this point of view the solubility in ammonia is due to the formation of a salt similar to that of carminic acid.

Well prepared purple solutions have a homogeneity scarcely less than that of the crystalloidal dyestuffs. The behavior toward mercury is another evidence of the correctness of the view upheld by Berzelius. Metallic mercury dissolves gold very easily, while the gold in purple is not attacked by mercury. The electrolysis of purple solutions resembles closely that of a complex, or that of a dyestuff dissolved by an electrolyte, such as Methyl Orange. Just as in the case of the last salt dimethylamidoazobenzolsulfonic acid is deposited on the anode in crystalline form, so is purpuric acid precipitated on the anode in form of a gel.

Nevertheless on the evidence we must abandon the view of Berzelius. It should be noted that mere traces of ammonia will dissolve large amounts of purple, three grams of ammonia suffice for 1000 g. of dehydrated purple. From this it would follow that purpuric acid must have an enormous molecular weight. Moreover purple will not pass through parchment paper during electrolysis as electrolytes do. Finally, methods for the preparation of purple solution settle the question for us.* A mixture of colloidal gold and colloidal stannic acid in correct proportions treated with dilute acid gives a precipitate that is identical in every way with purple solutions made according to the previously mentioned methods. One would scarcely expect the inactive gold to unite with the comparatively inactive stannic acid. In fact if submicroscopic gold particles are chosen for the preparation of synthetical purple solutions the particles may be seen under the ultramicroscope just as easily after the reaction as before the solutions were mixed. The absorption spectra of ordinary and synthetic purple solutions are identical. All this goes to show that the gold has not entered into chemical combination although the reactions have so materially changed. The analysis of the above arguments is important in colloidal chemistry because certain authors have used these same arguments in the case of many other colloids.†

* R. Zsigmondy: Liebigs Annalen, **301**, 375 (1898).

† R. Zsigmondy: Zur Erkenntnis der Kolloide, 56 (1905).

The peptisation of the purple of Cassius is also important for the explanation of this phenomenon. As long as the point of view of Berzelius was held peptisation could be attributed to the formation of a salt. Since this is no longer tenable we must accept some such explanation as has been given in the theoretical part of this book. See Chapter IV.

Substances Analogous to the Purple of Cassius

Allied to the purple of Cassius are those substances composed of colloidal metals and colloidal stannic acid. A good instance of this is silver purple. Silver nitrate and stannous nitrate form a blood-red solution that gradually turns brown and from which a reddish brown precipitate falls out. Ditte * mistook this for silver stannate, but L. Wöhler † has demonstrated that the substance is analogous to gold purple. Lottermoser ‡ has succeeded in preparing another silver purple synthetically by mixing colloidal silver and colloidal stannic acid. Acids throw out a dark violet precipitate that dissolves in alkali with a deep brown color. The same product may be obtained by mixing solutions of silver nitrate, stannic chloride and ammonium citrate.

According to L. Wöhler § an analogous platinum combination may be made from stannous chloride and platinum chloride. A blood-red color ensues that was formerly attributed to the presence of platinous chloride, but has since been shown to be finely divided metal. At sufficiently great dilution a brown precipitate falls out. This may be washed free from chlorides and then has the following composition:

$$PtSn_6O_{12}.$$

Other substances have been made by the same process and have the composition:

$$Pt(SnO_2)_8 \text{ and } Pt(SnO_2)_5.$$

These products have all the properties of colloids. They show the effects of ageing, when freshly prepared are soluble in ammonia or dilute hydrochloric acid, and after drying are scarcely at all soluble in concentrated hydrochloric acid. The red substance does not diffuse through membranes.

Another peculiar reaction might be noted. If made in strong hydrochloric acid solution the red platinum purple is soluble in ether and in ethyl acetic ether, so that it may be separated from the water by shak-

* A. Ditte: Annales de Chim. et de Phys. (5), **27**, 145–182 (1882); J. B., **343**, 1301 (1882).

† L. Wöhler: Koll.-Zeit., **7**, 248 (1910).

‡ A. Lottermoser: Anorganische Kolloide, 53. Stuttgart (1901).

§ L. Wöhler: Koll.-Zeit. 2, Suppl. **1**, 111, 53 (1907).

ing with these solvents. The ether solution leaves a residue soluble in water. It would seem that a stannic oxychloride plays the rôle of a protective colloid in this case, and that the ether modification does not form a complex crystalloid.

Metastannic Acid Containing Iron

In the purple of Cassius we have an amalgamation of the properties of both components. The colloidal gold is responsible for the color and a part of the optical properties, while most of the reactions are those of stannic acid. Only in case the gold is the larger portion of the purple does coagulation by electrolytes come into consideration. Toward other colloids both components exert the individual reactions of each. An interesting case has been observed by Lepéz and Storch.* When tin is dissolved in hot nitric acid metastannic acid is formed. If, however, ferric nitrate has been added to the nitric acid metastannic acid containing iron is formed, and this exhibits entirely different reactions from ordinary metastannic acid. As is well known, metastannic acid becomes insoluble if water is added to the mixture. If, however, the colloidal combination contains one atomic weight of iron to one of tin the mass will dissolve when it is diluted with water. When the stannic acid is present in larger proportions than the above the mass loses its solubility in water, but may be dissolved in concentrated hydrochloric acid.

Not only are the reactions of metastannic acid partially hidden by the mixture, but also those of iron oxide. If sufficient stannic acid is in the precipitate, ammonia will cause peptisation. This is contrary to the behavior of iron oxide, of course, because the latter is thrown out of solution by ammonia.

The property that stannic acid has of preventing the precipitation of many oxides such as those of bismuth, copper, lead, etc., and likewise the precipitation of phosphoric acid, is well known in analytical chemistry.

C. Colloidal Titanic Acid, Colloidal Zirconium Oxide and Colloidal Thorium Oxide

Colloidal titanic acid can be prepared by Graham's † method, *viz.*, the addition of ammonia to salts of titanium in solution. The precipitate is peptised by nitric acid and then dialyzed. The dialysis of the nitrate, a method followed by Biltz,‡ is applicable to the preparation

* C. Lepéz und L. Storch: Monatshefte f. Chemie, **10**, 283–294 (1889).
† Th. Graham: Annalen d. Chemie u. Pharmazie, **135**, 65–79 (1865).
‡ W. Biltz: Ber., **35**, 4431–4438 (1902).

of colloidal zirconium and thorium oxides, and indeed to all colloidal oxides of trivalent or quadrivalent metals. Nitrates of the bivalent metals are not sufficiently hydrolyzed to make this method possible in their case.

Colloidal Zirconium Oxide. — As already stated colloidal zirconium oxide is made by dialyzing the nitrate. Solutions having a concentration of about 17 per cent are dialyzed for 5 days. Hydrosols thus obtained contain particles that are charged positively, and give a precipitate with negative colloids. With gold in suitable proportions, for instance, a red precipitate comes down, which is analogous to the purple of Cassius. Biltz * states that the solution has decided protective properties. When HCl is employed the gold number has been found by Biltz,* and also by Behre † to be 0.05.

Zirconium oxychloride is hydrolyzed according to Ruer,‡ and the reaction may be hurried by a rise of temperature. The dialysis of such solutions gives a hydrosol of zirconium oxide. A further change in the solution results in the formation of metazirconic acid, and the reactions are accordingly different from the original hydrosol.

Both the oxychloride and the nitrate give a precipitate with oxalic acid, which precipitate is soluble in an excess of the reagent. This reaction does not take place in the presence of sulfates because of the formation of a complex in which the zirconium is in the anion. The probable formula is $K_2[ZrO(SO_4)_2]$. When, however, the solution is aged and hydrolysis has sufficiently progressed so that metazirconic acid has been formed, the presence of sulfates no longer serve to cover up the action of oxalic acid. In fact old solutions if warmed will give precipitates with sulfates that are soluble in an excess of the reagent. Freshly prepared zirconium oxychloride or nitrate solutions, on the other hand, give no precipitate with sulfate. These changes that take place on ageing are doubtless responsible for many discrepancies in the work of different investigators.

Colloidal Metazirconic Acid. — On boiling, the hydrosol of zirconic acid changes to metazirconic acid. For the preparation of the meta acid, metazirconium chloride may be employed. This latter substance is made by repeated evaporation of the oxychloride. By dialyzing the solution a milky liquid is obtained that closely resembles metastannic acid. Concentrated HCl produces a precipitate that is soluble in water. Concentrated solutions of alkali chloride behave similarly. The hydrosol is completely precipitated by sulfuric acid and the pre-

* W. Biltz: Ber., **35**, 4431–4438 (1902).

† P. Behre: Inaug.-Diss. Göttingen (1908).

‡ R. Ruer: Zeit. f. anorg. Chemie, **43**, 282–303 (1905).

cipitate is not at all soluble in an excess of the acid. The same is true of the action of sodium sulfate. The dehydrated residue of this hydrosol is amorphous and opaque in contradistinction to the transparent residue from ordinary zirconium oxide hydrosol.

The hydrogel of metazirconic acid is obtained by precipitating the metachloride with ammonia. It is not so voluminous as the ordinary variety and behaves differently on being heated. The latter glows on being heated while the former does not. The heat of reaction during the change from the ordinary form to the more stable is 9.2 cal.

Colloidal Thorium Oxide.—Colloidal thorium oxide obtained by dialyzing the nitrate is clear and neutral, but contains traces of nitrate.* On evaporation there remains a rubber-like lustrous mass that is not soluble in water. The hydrosol is very stable toward electrolytes; dilute HCl and even normal sodium chloride solution causes no reaction. More concentrated solutions of sodium chloride, or 30 per cent ammonium sulfate cause a precipitate. This stability is diametrically opposed to the great susceptibility of colloidal cerium or zirconium oxides. A peculiar preparation for thorium oxide is given by Cleve.† Thorium oxide evaporated down with HCl is not changed in outward appearance, but is, nevertheless, soluble in water and forms a turbid liquid. Szilard ‡ has made a stable hydrosol of thorium oxide by peptising a well washed sample of thorium hydrate with nitric acid. A. Müller§ obtained a reversible hydrosol by peptising the gel of thorium hydroxide with HCl at boiling temperature. The well washed gel is thrown out in boiling water and peptised by N/20 HCl. On evaporating this hydrosol a rubber-like residue remains that distends in water and forms a viscous liquid. This "mineralische Gummi" dries on paper to form a lustrous layer that will stick pieces of paper together as gum arabic does. This hydrosol reacts as a semicolloid, and its properties are probably due to excess of HCl used in peptisation which has not been removed by dialysis. As in the case of all positively charged colloids this hydrosol will precipitate all negatively charged colloids including colloidal gold.

Peptoids

Since the time of Graham ¶ it is well known that a certain analogy exists between peptone formation from egg albumin and inorganic peptisation. Szillard || has endeavored to elaborate on the analogy.

* *l. c.*

† P. T. Cleve: Bull. Soc. Chim. (2), **21,** 115–123. Paris (1874); J. B., 251 (1874).

‡ B. Szilard: Journ. de chim. phys., **5,** 488–494 (1907).

§ A. Müller: Koll.-Zeit. 2, Suppl. **1,** VI–VIII (1907).

¶ Th. Graham: Phil. Transact., 183 (1861); Liebigs Annalen, **121,** 45 (1862).

|| B. Szillard: Journ. de chim. phys., **5,** 495, 636–646 (1907).

Coagulated egg albumin digested with pepsine is changed into peptones and albumoses that have a greater degree of homogeneity than the original albumin. Likewise the hydrogels of different inorganic colloids may peptise with HCl or alkalis, and even with salts of the heavy metals. As an example of this may be cited Graham's iron oxide hydrosol. Szillard has shown that the peptisation with salts of the heavy metals is general, and that a whole series of new, mixed heterogeneous colloids may be obtained by peptising the hydrogel of one metal oxide with the salt of another having a high valence. These new hydrosols have been called by Szillard, peptoids. Two examples of the series have been chosen for purposes of illustration.

1. Uranium hydrate thorium peptoid.
2. Thorium hydrate uranyl peptoid.

The first is made by peptising uranyl hydrate with thorium nitrate; the second by peptising thorium hydrate with uranyl nitrate. The first is a delicate yellowish green, while the second is a dark reddish yellow. With regard to the preparation it should be noted that the hydrate must be well washed, whereby a suspension is formed. The solution of the nitrate is raised to the boiling point and gradually added to the suspension.

The reaction itself may be explained on the following grounds. The first portions of the hydrogel are either peptised by the cathion of the salt, or dissolved by the nitrate to form a basic salt. These combinations next form adsorption complexes with more oxide, the anions dissociate off and the complex is therefore positively charged. That different products are formed is evidenced by the variety of colors in the hydrosols. Coagulated egg albumin may also be peptised by the salts of the heavy metals.

D. Colloidal Iron Oxide

Graham's * method for preparing colloidal iron oxide is to dissolve iron hydroxide in a solution of ferric chloride and then dialyze. Krecke † dialyzed a dilute solution of ferric chloride, while Biltz ‡ employed the nitrate. Colloidal iron oxide having somewhat different properties has been made by Péan de St. Gilles § by continued boiling of a solution of ferric acetate. Graham has called these solutions colloidal metairon oxide.

The preparation, according to the method of Graham, is colored deep brown, is comparatively free from electrolytes, but always contains

* Phil. Transact., 183 (1861); Liebigs Annalen, **121**, 45 (1862).

† F. Krecke: Journ. f. prakt. Chemie (2), **3**, 286–306 (1871).

‡ W. Biltz: Ber., **35**, 4431–4438 (1902).

§ Péan de St. Gilles: Compt. rend., **40**, 568–571, 1243–1247 (1855).

traces of chlorides that cannot be completely removed. Most electrolytes cause precipitation, but dilute acids merely render the hydrosol more stable. Hydrosols with properties similar to those of Graham and having a concentration of about 5 per cent may be had on the market. Merck handles a 10 per cent preparation that contains relatively more chloride than does the 5 per cent preparation.

The brown color of ferric acetate becomes gradually brick red on boiling and the peculiar taste of ferric acetate becomes more like that of acetic acid. Hydrosols prepared by Graham's method contain smaller particles than those of Péan de St. Gilles. In the hydrosols on the market one is able to discern, beside the individual particles, homogeneous light cones. On diluting, these cones gradually fade away without being resolvable. Hydrosols from ferric acetate give much more intense light cones, and contain, therefore, much larger particles. Coehn * has shown that the iron oxide hydrosols mentioned above are all charged positively; but recently Fischer † has prepared a negatively charged one.

Reactions of Colloidal Iron Oxide. — Colloidal iron oxides obtained from the acetate are turbid in reflected light and clear in transmitted. Sulfuric acid or its salts coagulate the hydrosol immediately, and the precipitate is not soluble in concentrated acid in contradistinction to the precipitate from Graham's solutions. When the hydrosol is poured into concentrated acid a precipitate is formed that is again dissolved by water. There exist several analogies between the hydrosol of metastannic acid and those of these ferric acetate hydrosols; this accounts for the name, metairon oxide. The hydrosol deserves more elaborate investigation; the apparent isomerism of the two modifications is probably due to the difference in the size of the particles.

Graham's iron oxide differs from the meta variety in that the former is more stable and its precipitate is more soluble in acids. Colloidal iron oxide on the market has properties that lie between these two extremes. It is precipitated by moderately concentrated HCl but the solid gradually goes into solution again to form a chloride. This colloid therefore bears the same relation to Graham's and metairon oxide that colloidal stannic oxide prepared by the author's method bears to the α and β varieties.

Reference may be made to a remark of Graham ‡ that is pertinent to all colloids. Where it is solely a case of some interchange or reaction between the particles the process may take place quickly, such as the

* A. Coehn: Zeit. f. Elektrochemie, **4**, 63–67 (1897–98).

† H. W. Fischer und E. Kusnitzky: Biochem. Zeit., **27**, 311–325 (1910).

‡ Th. Graham: Liebigs Annalen, **121**, 70–71 (1862).

precipitation of iron oxide by electrolytes. On the other hand, where true chemical reactions are involved, colloids demand an appreciable (sometimes a long) time for their completion. This is exemplified by the slow dissolution of the precipitated iron oxide in the acidified liquid.

Other Reactions of Colloidal Iron Oxide.—The characteristic iron taste, or ink taste, is entirely lacking, due doubtless to the scarcity of the ferric ion in the colloidal solution. The hydrosol gives only a rough feel on the tongue. Another evidence * that the ferric ion is present only in extremely small amount in well dialyzed hydrosols is the fact that potassium ferrocyanide gives no Prussian blue, although this is a very delicate test for ferric ion. Silver nitrate fails to show the presence of the chloride ion. This is of special interest because Ruer,† and Hantzsch and Desch,‡ all have demonstrated that some chloride is present. The two latter authors attribute the failure of silver nitrate to show a chloride reaction to the formation of a chloride complex. Ruer, however, ascribes the phenomenon to a protective action of the colloidal iron oxide. That is to say, the particles of silver chloride do not become large enough to cause a turbidity. For instance, a solution containing 0.752 g. Fe_2O_3, 0.220 g. Cl in 100 cc. gives only a faint opalescence with silver nitrate. If the solution is boiled with nitric acid so that the iron is dissolved, silver chloride is at once apparent. Ruer proved that the hydrosol actually contains the chloride ion by dialyzing without changing the water. The outer vessel contained 0.0056 per cent Fe_2O_3 and 0.0760 per cent Cl; while the inner contained 0.7032 Fe_2O_3 and 0.1388 per cent Cl. The outer liquid gave a good test for chloride ion while the inner did not. As there must be an equilibrium between the chloride ion in the two liquids it is clear that the non-appearance of silver chloride in the inner vessel must be due to some protective action.

A series of interesting and theoretically important researches have been carried out by Duclaux § during his work on Hardy's precipitation law. He experimented on solutions of colloidal copper, ferrocyanide and colloidal iron oxide. Different sorts of colloidal iron oxide were treated with a series of electrolytes, with the result that 10 cc. of the hydrosol were precipitated by almost equivalent quantities of anions regardless of the valency. For instance, 10 cc. of a hydrosol having 0.0203 gram atoms of iron in a liter, 0.00166 gram atoms of Cl

* H. W. Fischer und E. Kusnitzky: Biochem. Zeit., **27**, 311–325 (1910).
† R. Ruer: Zeit. f. anorg. Chemie, **43**, 85–93 (1905).
‡ A. Hantzsch und C. Desch: Liebigs Annalen, **323**, 28–31 (1902).
§ J. Duclaux: Journ. de Chim. Phys., **5**, 29–56 (1907).

in a liter required for coagulation the gram equivalents of various anions given in Table 24.

TABLE 24

$17 \cdot 10^{-6}$	Gram equivalents	$SO_4^{=}$
$16.5 \cdot 10^{-6}$	" "	citrate ion
$15.2 \cdot 10^{-6}$	" "	$CrO_4^{=}$
$17 \cdot 10^{-6}$	" "	$CO_3^{=}$
$19 \cdot 10^{-6}$	" "	$PO_4^{\equiv}$
$16.1 \cdot 10^{-6}$	" "	OH^{-}
$13 \cdot 10^{-6}$	" "	$FeCy_6^{==}$
$1880 \cdot 10^{-6}$	" "	NO_3^{-}

It was further shown that the amount of sulfate or hydroxide ion necessary for precipitation was almost equivalent to the chloride content of the hydrosol. The relations for a solution of iron oxide containing $203 \cdot 10^{-6}$ gram atoms of iron are given in Table 25.

TABLE 25

Gram atom Cl.	Gram equivalent.		
	SO_4^{-}	OH^{-}	NO_3^{-}
$17 \cdot 10^{-6}$	$17 \cdot 10^{-6}$	$16 \cdot 10^{-6}$	$1880 \cdot 10^{-6}$
$8 \cdot 10^{-6}$	$6.8 \cdot 10^{-6}$	$6.6 \cdot 10^{-6}$	$440 \cdot 10^{-6}$
$4.1 \cdot 10^{-6}$	$4 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$70 \cdot 10^{-6}$
$2.8 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	$2.2 \cdot 10^{-6}$	$36 \cdot 10^{-6}$

There seems to be no equivalent relation for the nitrate ion. The same want of relation also exists for sodium chloride as may be seen in Table 26.

TABLE 26
IRON OXIDE HYDROSOL

With gram atom Cl.	Precipitated by gram equivalents.	
	$SO_4^{=}$	NaCl
11	13	2000
7.2	7.2	170
4.8	3.4	75
1	0.9	6

With the exceptions of the nitrate ion and sodium chloride, equivalent quantities of the anions cause the same effect. That the quantities are not exact is to be expected when one considers that the experimental error is large owing to the fact that precipitation depends somewhat on the manner of adding the electrolyte.

The Schulze-Hardy precipitation law does not hold for the nitrate ion nor for sodium chloride. In explanation the assumption may be

made that colloidal iron oxide is a solution of an oxychloride having a high molecular weight, the cathion of which unites with the anion of the electrolyte to form an insoluble precipitate. Or one may assume that the iron ultramicrons have adsorbed the cathion of the oxychloride as represented on page 79. The latter assumption is the more general and will be dealt with at length.

The adsorbed cathion, the nitrate and chloride of which are soluble, gives the positive charge to the ultramicrons and is responsible for the stability of the hydrosol. In order to cause the precipitation of the insoluble union (Fe-complex-cathion)$_m$ (anion)$_n$, it will be necessary to add enough of the reagent to correspond to the chloride ion in solution, hence the equivalence between the precipitating anion and the chloride content of the colloid. To make this clear let us assume that the absorbed cathion has the formula, $Fe_2O_2^{++}$ and the undissociated salt the formula, $Fe_2O_2Cl_2$. The following formulas would therefore represent the adsorption of the cathion by the ultramicrons and finally the neutralization of the complex by the anion of the addition agent.

$$\boxed{Fe_2O_3} + Fe_2O_2^{++} = \boxed{Fe_2O_3} \cdot Fe_2O_2^{++}$$

$$\boxed{Fe_2O_3} \cdot Fe_2O_2^{++} + 2\,OH^- \rightarrow \downarrow \boxed{Fe_2O_3}\, Fe_2O_2\,(OH)_2$$

The hydroxide ion may be replaced by SO_4^{--}, CrO_4^{--}, etc.

According to the assumption the nitrate and the chloride are much more soluble so that more of these precipitating agents must be added to cause coagulation.

Conductivity of Colloidal Iron Oxide

Malfitano * has shown that solutions of potassium or iron chloride will pass through collodion membranes without causing any change in conductivity. Duclaux † has investigated the conductivity of colloidal solutions making use of collodion membranes. He has shown that colloidal iron oxide made by Graham's method, and containing 0.032 gram atoms of iron per liter, gives a colorless filtrate if filtered through a collodion membrane.

The original solution had the conductivity...........	$113 \cdot 10^{-6}$
The filtrate had the conductivity....................	$82 \cdot 10^{-6}$
The residue, $\frac{1}{10}$ of the original, had the conductivity..	$280 \cdot 10^{-6}$

The increase in the "micellen" has increased the conductivity.

That the intermicellular liquid is not changed by passing through the membrane is shown by the following table.

* G. Malfitano: Compt. rend., **139**, 1221 (1904).

† J. Duclaux: Compt. rend., **140**, 1468–1470, 1544–1547 (1905); Koll.-Zeit., **3**, 126–134 (1908)

TABLE 27

Time of measurement.	Conductivity of the filtrate in arbitrary units.
At the beginning	100
Concentration increased 4 fold	99
" " 6 "	101
" " 24 "	106

Not until the end is there any increase in the conductivity. This result is corroborated by some researches in the author's laboratory by Dr. Bachmann. From this it is clear that the adsorption of the electrolyte by the membrane is negligible, a result that is important in both filtration and in measurements on osmotic pressure. It renders an objection raised by Lottermoser invalid.* Recently Lottermoser has become convinced that the filtration method of studying adsorption within a liquid is suitable.† An article by Wo. Ostwald ‡ also corroborates this.

Osmotic Pressure. — Duclaux § has shown that colloidal iron oxide exhibits an osmotic pressure against its filtrate, that it increases with the concentration but is not proportional to the latter. When the concentration increased from 1 to 18 the pressure rose in the ratio of 1 to 80. The cause for this want of proportion is not yet very well understood, but Duclaux has offered a somewhat plausible explanation.¶ He has also shown that the osmotic pressure of iron oxide hydrosol sinks with a rise of temperature. The author carried on an experiment for over one and one-half years and found at regular intervals that a rise in temperature to 50° C. caused a fall in the pressure of about 15 mm. As the temperature was lowered the column gradually went up again. There is a gradual decrease in the osmotic pressure that is partly accounted for by the changes that go on in the colloid, *viz.*, the formation of larger particles from the smaller. Submicrons could be easily seen toward the end of the experiment.

Magnetic-optical Investigations

Form of the Ultramicrons. — Majorana || has observed that colloidal iron oxide on a magnetic field exhibits the properties of uni-

* A. Lottermoser: Zeit. f. phys. Chemie, **60,** 451–463 (1907).

† A. Lottermoser und P. Maffia: Ber., **43,** 3613–3618 (1910).

‡ Wo. Ostwald: van Bemmelen-Gedenkboek, 267–274 (1910).

§ J. Duclaux: Compt. rend., **140,** 1544 (1905).

¶ J. Duclaux: Journ. de Chim. Phys., **7,** 405–446 (1909).

|| Qu. Majorana: Rendic. R. Accad. Lincei, **11, 1,** 374, 463, 531; **11, 90,** 139 (1902).

axial crystals. The hydrosol of iron oxide in the field of a powerful electromagnet, and traversed by a light ray at right angles to the lines of force, exhibits double refraction sometimes as great as that of quartz. The double refraction disappears again when the magnet is switched out of the circuit. The amount of the double refraction depends upon the age of the hydrosol.

Schmauss * called attention to the fact that this was a general property of colloids, and assumed that the magnet caused an orientation of the particles. Cotton and Mouton † with the aid of the ultramicroscope corroborated the observations of Schmauss, accepted his theory and extended its application materially. They found that ultrafiltration through collodion membranes increased the double refraction of the colloid, while the filtrate remained inactive. It is found that coagulation under ordinary circumstances gives an inactive gel, but that if the coagulation takes place in the magnetic field the gel exhibits a permanent double refraction even after the removal of the magnet. Finally, the turbidity and the double refraction become greater with the age of the hydrosol; this change may be hastened by raising the temperature. On heating four hours at 100° C. the double refraction increases fortyfold. The turbidity and the viscosity increase during the warming, therefore the greater the particles the greater the double refraction. Some hydrosols prepared by electrical colloidation contained particles that could be seen under an ordinary microscope. These particles were long and became orientated in the magnetic field, and simultaneously the hydrosol exhibited double refraction. It seems plausible therefore, that this phenomenon is due to the orientation of the ultramicrons that are lamellar or rod-shaped.‡ Cotton and Mouton have demonstrated that the rods or flakes do not form threads.

It is now quite clear why the larger particles cause a greater effect than the smaller. The brownian movement tends to disturb the orientation and the smaller ultramicrons having a much greater rate of motion than the larger do not become orientated sufficiently to cause pronounced double refraction. From the researches of Cotton and Mouton the question whether the position of the particles alone, or whether the particles themselves, cause double refraction, must be answered in favor of the latter assumption.

* A. Schmauss: Drudes Annalen d. Phys. (4), **12,** 186–195 (1903).

† A. Cotton et H. Mouton: Compt. rend., **141,** 317, 349 (1905); Soc. fr. de phys., **17,** Nov. (1905). Les ultramicroscopes, etc., Chap. VIII. Paris (1906).

‡ O. Wiener: Physikal. Zeit., **5,** 332–338 (1904). Lord Rayleigh: Philos. Magaz. (**5**), **34,** 481–502 (1892). Kerr: Report of Brit. Assoc. Glasgow, 568 (1901). F. Braun: Physikal. Zeit., **5,** 199–203 (1904).

The researches of Cotton and Mouton are of great importance for the theory of colloidal chemistry. We have here for the first time direct evidence that a colloid closely resembling the lyophiles contains particles the form of which is not that of a sphere, but rather that of tiny crystals. Nägeli * has explained the optical and many other properties of colloids on the grounds that they consist of anisotropic ultramicrons having a great resemblance to crystals.

Iron Oxide Hydrogels. — Van Bemmelen † has investigated the dehydration of the gel of iron oxide and obtained curves similar to those of silicic acid. The water content decreases continuously with the decrease of vapor tension. The transition point is less pronounced than in the case of silicic acid gel. The course of the dehydration and the readsorption is shown by the curves in Fig. 29.

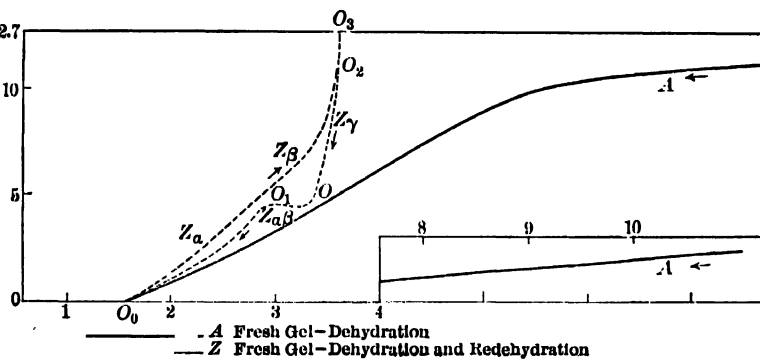


FIG. 29. Dehydration of Iron Oxide Gel according to van Bemmelen.

The curves do not indicate the existence of a hydrate in the hydrogel. Colloidal iron oxide, however, goes over very easily into crystalline hydrates, ‡ for example Goethit with the formula, $Fe_2O_3 \cdot H_2O$. The water content remains constant even up to 79° C. It differs markedly from the gel in that it has no tendency toward adsorption. This is doubtless due to the finer state of subdivision and to the reduced surface.

The Adsorption of Arsenious Acid. — Biltz § has studied the adsorption combination of arsenious acid with colloidal iron oxide. The complex was previously given a definite chemical formula and was regarded by Bunsen, who discovered that the hydrogel of iron was an

* C. v. Nägeli und S. Schwendener: Das Mikroskop., 2. Aufl. Leipzig (1877). C. v. Nägeli: Theorie der Gärung, 121 ff. München (1879).

† van Bemmelen: Zeit. f. anorg. Chemie, **20,** 185–211 (1899).

‡ van Bemmelen und E. Klobbie: Journ. f. prakt. Chemie, **46,** 497–529 (1892); Zeit. f. anorg. Chemie, **20,** 185–211 (1899). H. W. Fischer: Zeit. f. anorg. Chemie, **66,** 37–52 (1910).

§ W. Biltz: Ber., **37,** 3138–3150 (1904).

antidote for arsenic poisoning, as a basic ferriarsenite. Biltz has shown, however, that the curve for the taking up of arsenious acid by colloidal iron oxide is quite similar to the adsorption curves of van Bemmelen. We have to do here with an adsorption phenomenon and not with a chemical compound, Fig. 30. The arsenic content varies with the concentration of the arsenious acid in solution, as may be seen from Fig. 30.

E. Colloidal Aluminium Oxide and Chromium Oxide

Aluminium Oxide.—Compared to colloidal iron oxide aluminium does not offer anything new. Two modifications are known, one of which may be prepared according to Crum * by boiling the acetate. The hydrosol is coagulated by acids and is difficultly soluble in an excess of the reagent, resembling metairon oxide in this respect. Small amounts of salts are necessary for precipitation, and it is not reactive

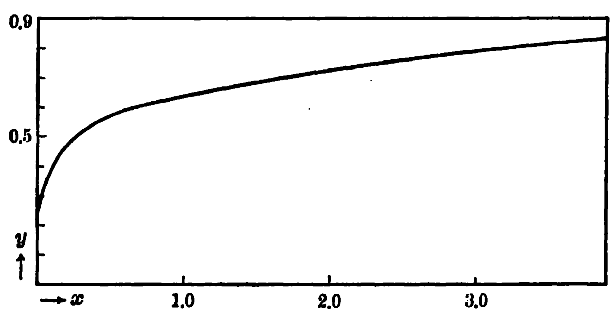


Fig. 30.

as a mordant for dyes. Graham has called this the meta variety of aluminium oxide. Graham's † hydrosol is made by dissolving aluminium oxide gel in a solution of aluminium chloride and dialyzing. The product is very sensitive toward electrolytes and reacts as a mordant for dyes in a manner similar to the salts of aluminium. It is also sensitive to concentrating by evaporation. A one-half per cent solution of the hydrosol may be boiled without coagulating, but on evaporating to one-half the volume precipitation takes place suddenly. If drops of the hydrosol are placed on red litmus paper coagulation sets in and blue rings are formed around the outside. Well dialyzed hydrosols may be coagulated by most electrolytes, by a small amount of spring water, and even by shaking or pouring into another vessel. Dilute acids coagulate them but the precipitate is soluble in an excess in contradistinction to the meta variety.

* W. Crum: Journ. f. prakt. Chemie, **61,** 390 (1854).

† Th. Graham: Liebigs Annalen, **121,** 41 (1862).

A reversible colloidal aluminium oxide has been made by A. Müller * by peptising freshly precipitated aluminium hydroxide with HCl. A solution of aluminium chloride containing 1.124 g. Al_2O_3 in 50 cc. was treated with ammonia, washed as quickly as possible with water, and put into 250 cc. of water in a flask. The whole was brought to a boil, and 20 cc. of N/20 HCl added drop by drop. The amount of acid added is only about $\frac{1}{78}$ of that necessary to form aluminium chloride. The hydrosol thus prepared is quite stable, and leaves a precipitate that is soluble in water. If the amount of water is small a viscous liquid is formed that resembles gum arabic. It possesses good protective power and has a gold number of 0.02 to 0.04. The stability is probably caused by the large amount of peptising material that has not been removed by dialysis.

Colloidal Chromium Oxide.—The hydrosol of chromium oxide is made similarly to that of colloidal iron oxide,† by the peptisation of the hydroxide by means of chromium chloride. The solution is deep green and is somewhat more stable than that of aluminium oxide. According to H. W. Fischer ‡ the alkali solution of the hydrogel is also a colloid. Colloidal chromium oxide should be more closely studied.

The older belief that chromium oxide could be precipitated by the acetate method just as iron oxide is, has been shown by Schiff § to be only partially true. Reinitzer ¶ has investigated the abnormal behavior of chromium in this regard, and the results are of importance in analytical chemistry. He found that chromic salts give no precipitate with sodium acetate, but on the contrary the presence of this element could in some degree prevent the precipitation of iron oxide by the acetate method. He was able to show that the product obtained by boiling pure chromium acetate had a distinct protective effect on the precipitation of iron oxide by alkalis and alkali carbonate. It is not a stretch of the imagination to assume that the action is similar to that of gelatin on colloidal gold. It is also possible, however, to ascribe the phenomenon to the formation of complexes containing iron, chromium, and acetate.|| The question has not yet been answered experimentally.

* A. Müller: Koll.-Zeit., **2,** Suppl. **1,** VI–VIII (1907); Zeit. f. anorg. Chemie, **57,** 312 (1908).

† Th. Graham: Liebigs Annalen, **121,** 52 (1862).

‡ H. W. Fischer und W. Herz: Zeit. f. anorg. Chemie, **31,** 352–358 (1902). H. W. Fischer: *Ibid.*, **40,** 39–53 (1904).

§ H. Schiff: Liebigs Annalen, **124,** 168 ff. (1862).

¶ B. Reinitzer: Sitzungber. d. Akad. d. Wiss. Wien, **85, 11,** 808–824 (1882).

|| A. Recoura: Compt. rend., **129,** 158–161, 208–211, 288–291 (1899); Chem Centralbl., II, 416, 475, 523 (1899).

F. Other Colloidal Oxides

Colloidal Tungstic and Colloidal Molybdic Acids

Both colloids according to Graham are reversible and can be made by dialyzing the acidified solutions of the corresponding salts of sodium.* The hydrosol of tungstic acid is prepared by the addition of a slight excess of HCl to a 5 per cent solution of sodium tungstate. The liquid is put in the dialyzer and HCl added every two days until all the alkali is removed. The purified acid is not coagulated by acids, salts, nor by alcohol. The residue on evaporation is in the form of glass-like flakes that stick to the vessel so tenaciously that sometimes it is impossible to remove them without breaking the surface of the porcelain dish. The residue may be heated to 200 degrees without losing its solubility, but in the neighborhood of red heat 2 to 3 per cent of water comes off and the mass becomes insoluble. With about one-fourth its weight of water the gel forms a liquid upon which glass will float. With sodium carbonate the solution effervesces. The taste is not sour but bitter and astringent. It prohibits the coagulation of liquid silicic acid probably because of the formation of silicon tungstic acid.

It is difficult to prepare the colloid free from alkali. Sabanejeff † was inclined to believe that Graham's preparation was a tungstate, but the recipe provides for the removal of the alkali. L. Wöhler ‡ dialyzed a sample made by Graham's method and found that tungstic acid diffuses much more slowly than colloidal molybdic acid. After three weeks dialysis the outer liquid, which had not been renewed, contained about one-third as much tungstic acid as the inner liquid. When left standing for 13 months, beautiful double refracting crystals of tungstic acid came out. Pappadà § prepared an unstable hydrosol by dialyzing a solution of tungstic acid in oxalic acid. This sample would coagulate on mere warming. Recently Müller ¶ obtained a hydrosol sensitive to electrolytes by diluting an alcohol ether solution of $WOCl_4$, with water. Lottermoser ‖ has made a sample with sodium tungstate supersaturated with HCl. According to the concentration hydrosols are obtained having a degree of dispersion varying from suspensions to apparently homogeneous solutions.

* Th. Graham: Poggendorffs Annalen, **123**, 539–540 (1864).

† A. Sabanejeff: Journ. d. russ. phys.-chem. Ges., **27**, 53 (1895); **29**, 243 (1897). Ref. Koll.-Zeit., **3**, 236 (1908).

‡ Lothar Wöhler: Koll. chem. Beihefte, **1**, 454–476 (1910).

§ N. Pappadà: Gazzetta chimica ital., **32**, **11**, 22–28 (1902).

¶ A. Müller: van Bemmelen-Gedenkboek, 416–420 (1910).

‖ A. Lottermoser: *Ibid.*, 152–157.

Colloidal Molybdic Acid. — This colloid may be made according to Graham by the treatment of sodium molybdate with HCl. The acid liquid may gelatinize after a time on the dialyzer, but becomes liquid again as soon as the salts have diffused away. After repeated addition of HCl and diffusion lasting several days about 60 per cent of the molybdic acid remain. The solution is yellow, astringent, acid to litmus, and possesses great stability. The dried residue has the same appearance as that of tungstic acid.

All investigators have not been successful in preparing a reversible molybdic acid hydrosol according to the method of Graham. Bruni and Pappadà * were unable to prepare any hydrosol by this method because the molybdic acid diffused through the membranes. This behavior recalls that of silicic acid at times. L. Wöhler * followed the method as given and obtained a dilute liquid that resembled the electrolytes in that it diffused through parchment paper, although much more slowly. Nevertheless it was optically inhomogeneous and had the colloidal property of being precipitated with gelatin. Graham's molybdic acid may therefore be considered a semicolloid and represents that class of substances that are on the boundary between the two great divisions, colloids and crystalloids.

Both tungstic and molybdic acids according to Graham form a number of crystallized salts with alkalis. These can be coagulated by heating for some time with HCl. According to Rosenheim and Bertheim * the dihydrate dissolves in water to form a crystalloidal solution capable of great supersaturation. The hydrate possesses a distinct solubility. None of the solutions give a precipitate of molybdic acid on cooling.

In the strongly supersaturated solution the same two authors have made molecular weight determinations and obtained values from 576 to 610. The substances in solution are highly dissociated and diffuse through parchment paper. They have suggested the presence of $H_2Mo_8O_{25}$, the molecular weight of which would be 1170. The smaller experimental value is due to the dissociation. Rosenheim and Davidsohn * found that on concentrating the supersaturated solution at about 50 degrees by evaporation a well-crystallized difficultly soluble monohydrate was obtained. If the concentration took place under 20 degrees over sulfuric acid a glassy residue remained that contained 12.3

* G. Bruni e N. Pappadà: Atti della R. Accad. Lincei Roma (**5**), 354–358 (1900); Gazzetta chimica ital., **31**, **1**, 244–252 (1901).

† Lothar Wöhler: Koll.-chem. Beihefte, **1**, 454–476 (1910).

‡ A. Rosenheim und A. Bertheim: Zeit. f. anorg. Chemie, **34**, 427–447 (1903).

§ A. Rosenheim und J. Davidsohn: Zeit. f. anorg. Chemie, **37**, 314–325 (1903).

per cent of water. This residue was soluble in water and formed an opalescent hydrosol, from which a precipitate could be obtained with alkalis or acids.

Rosenheim and Davidsohn conclude from their experiments that Graham's acid was not a colloid but consisted chiefly of the dihydrate. The molecular weight determinations favor this point of view, for Sabanejeff * obtained 620 while Rosenheim and Bertheim, as already stated, found the values 576 to 610. Nevertheless the solutions of these investigators and those of Graham do not appear to be exactly alike because the latter obtained his product on the dialyzer while the solutions of the other authors mentioned passed freely through the membranes. The pronounced property of molybdic acid to polymerize and change renders the existence of a colloidal modification, having the properties of Graham's preparations, not improbable. Too great weight should not be laid on the molecular weight determinations for similar relations exist in the case of the dyestuffs, *e.g.*, Congo red. The stability in the presence of electrolytes is also no evidence of the crystalloidal state, because there are a great many reversible colloids that have this property to a large degree.

Colloidal Tungsten and Molybdenum Blue. — Tungsten and molybdenum blue are likewise reversible colloids. They were employed by Biltz † as inorganic dyes in an investigation that proves that inorganic colloids may be adsorbed by fibers just as ordinary dyestuffs. Silk for instance is dyed directly. Instructive also is the behavior of molybdenum blue toward animal charcoal. Although the former is a reversible colloid it is completely adsorbed by the charcoal so that the filtrate is quite clear. Biltz ‡ has shown that both these two colloids are charged negatively and therefore precipitate positive colloids.

Dumanski § has determined the molecular weight of the crystalloidal blue molybdenum oxide obtained by the method of G. Marchetti,¶ and has found the value 440. The formula is supposed to be $Mo_3O_8 \cdot 5\,H_2O$. When this solution is treated with salt colloidal molybdic acid is formed.

Preparation of Molybdenum Blue. — Biltz treated the acidified solution of ammonium molybdate with hydrogen sulfide. Dumanski dissolved 15 g. of ammonium molybdate in 400 cc. water, added 100 cc. of 3 to 4 $n H_2SO_4$, and reduced the boiling solution with hydrogen

* A. Sabanejeff: Ber., **23**, R., 87 (1890); Journ. d. russ. phys.-chem. Ges., **21**, 515–525 (1889).

† W. Biltz: Nachr. d. Kgl. Ges. d. Wiss. Göttingen, Math.-phys. Kl.; 18–32 (1904), 46–63 (1905).

‡ W. Biltz: Ber., **37**, 1095–1116 (1904).

§ A. Dumanski: Koll.-Zeit., **7**, 20–21 (1910).

¶ G. Marchetti: Zeit. f. anorg. Chemie, **19**, 391–393 (1899).

sulfide. After filtration the colloid was dialyzed for three days. According to Dumanski crystallized MoO_3 can be obtained by boiling a suspension of purified MoO_3 with an excess of metallic molybdenum.

Several Other Colloidal Oxides

Colloidal vanadium pentoxide is negatively charged and according to Biltz * can be made by treating ammonium vanadate with HCl. The precipitate is washed until it goes into solution and then it is dialyzed. The hydrosol is colored yellow. Concentrated solutions coagulate easily.

Among the other oxides that might be mentioned are manganese † hydroxide studied by van Bemmelen,‡ cobalt oxide prepared by Müller,§ bismuth, lead, ceri-copper oxide, etc., and the many oxides of the platinum group studied by L. Wöhler and Ruff.¶

Before going to the discussion of colloidal sulfides a few words will be devoted to a group that plays an important part in analytical chemistry. It is well known that certain organic substances containing the hydroxyl group prevent the precipitation of iron and copper hydroxides. This property is possessed by sugar, glycerin, etc. Graham || showed by dialysis that these substances formed colloids, and that the oxide, or saccharate as the case might be, remained on the membrane, while the electrolytes passed through. Such colloids have been made by Grimaux ** by means of manniterythrite, glycerin, tartaric acid, etc., in a sodium hydroxide solution.†† Beside the iron oxide the dialyzer contained small amounts of alkali and organic substances, that doubtless in combination with the oxide formed a protective colloid and prevented the precipitation of the remainder of the iron. Such colloids as these cause Lea's colloidal silver to be soluble.

* W. Biltz: Nachr. d. Kgl. Ges. d. Wiss. Göttingen, Math.-phys. Kl., 51 (1905).

† Journ. Am. Chem. Soc., **37,** 1079.

‡ van Bemmelen: Journ. f. prakt. Chemie (**2**), **23,** 324–349, 379–395 (1881).

§ A. Müller: Koll.-Zeit., **2,** Suppl. **1,** VI–VIII (1907); Zeit. f. anorg. Chemie, **57,** 315 (1908).

¶ Z. B. L. Wöhler und W. Witzmann: Zeit. f. anorg. Chemie, **57,** 323–352 (1908). O. Ruff und F. Bornemann: *Ibid.*, **65,** 429–456 (1910) u. a.

|| Th. Graham: Liebigs Annalen, **121,** 51 (1862).

** E. Grimaux: Compt. rend., **98,** 1485–1488; J. B. 1884, 148.

†† H. W. Fischer: Biochem. Zeit., **27,** 311–325 (1910).

CHAPTER VIII

COLLOIDAL SULFIDES

THE tendency of the sulfides of the heavy metals to go through the filter while washing is known to every analytical chemist. In this manner larger subdivisions nearing the suspensions are obtained. Hydrosols of sulfides, exactly as in the case of the metals, may be prepared in all possible degrees of subdivision. This accounts for the want of uniformity in results obtained by the various authors. In fact it was this want of uniformity, and the gradual change of properties with the size of the particles that led to the discovery of the discontinuity of colloidal solutions.

The straw-colored liquid that is obtained by conducting H_2S into arsenious acid was regarded by Berzelius as a solution of arsenious sulfide. Later he remarked that the arsenious sulfide was probably in suspension because it fell out on standing. Schulze,* on the other hand, obtained solutions which were so stable that they no longer gave a precipitate on standing, and therefore decided that he had hydrosols similar to those described by Graham. The solutions were clear in transmitted light, while the more concentrated showed light diffusion in reflected light. Schulze regarded this as fluorescence.

Colloidal sulfides have been the subject of many important physicochemical investigations especially with regard to coagulation. Working with arsenious sulfide Picton and Linder † discovered, and Whitney and Ober ‡ elaborately determined, that equivalent quantities of cathions were necessary to precipitate the colloid.

Pure colloidal sulfides are as a rule rather unstable, sometimes even the dilute solutions cannot be kept. They are charged negatively and their color is generally that of the precipitated sulfide itself. Some are yellow while others are dark olive green, deep brown or black.

Colloidal Arsenious Sulfide

The hydrosol of arsenious sulfide was known to Berzelius but was first thoroughly investigated by Schulze.† The latter made his solu-

* H. Schulze: Journ. f. prakt. Chemie (**2**), **25**, 431–452 (1882).

† H. Schulze: Journ. f. prakt. Chemie (**2**), **25**, 431–452 (1882). H. Picton, Ders. und S. E. Linder: Journ. Chem. Soc., **61**, 114–172 (1892); **67**, 63–74 (1895).

‡ W. R. Whitney und J. E. Ober: Zeit. f. phys. Chemie, **39**, 630–634 (1902).

tions by conducting H_2S into a solution of arsenious acid. He demonstrated that salts of univalent cathions had the least pronounced precipitating effect while the trivalent cathions had the greatest. The bivalent occupied an intermediate position. According to Hardy this law has an application in the case of the precipitation of positively charged colloids by anions. As already stated on page 54 the law is not without exceptions, especially where protective effects play a part.

Schulze found that concentrated solutions gave larger particles than the more dilute. Picton and Linder also found that solutions having different degrees of dispersion could be prepared. They obtained four grades which they called α, β, γ, δ. The α variety contained the largest particles while δ was the finest subdivision. α particles could be detected with an ordinary microscope and were found to be in rapid motion, the Brownian movement. By means of unglazed porcelain filters the α and β particles could be easily separated from the liquid, while δ particles passed through. Solutions of the latter exhibited the property of diffusion and osmotic pressure. In this series of experiments it was shown for the first time that the properties of colloidal solutions became more and more like those of crystalloidal solutions as the dispersion became greater. However even the finest subdivisions of Picton and Linder revealed themselves to be inhomogeneous.

Picton and Linder also demonstrated that during the precipitation by electrolytes a portion of the latter was carried down with the precipitate. In other words negatively charged colloids carried down cathions while positively charged colloids adsorbed the corresponding amount of the anion that caused the coagulation. In the case of arsenious sulfide calcium was in the precipitate when calcium chloride was employed for the coagulation, and a corresponding amount of hydrogen ion was found in the liquid; that is the liquid became acid. The calcium could not be washed out of the precipitate, but could be replaced by strontium, and the latter in turn by barium. Van Bemmelen had previously found similar relations to hold for soils.

Whitney and Ober showed clearly that the amount of the various cathions necessary for precipitation was exactly equivalent. This result is of theoretical importance because from the amount of cathion held in the precipitate we can calculate the electric charge on the particles if we but know the number in a liter.

Other Sulfide Hydrosols

A large number of colloidal sulfides of the heavy metals have been prepared by Spring * and Winssinger,† and Schneider.‡ One can distinguish three different methods of preparation.

1. Precipitation of the sulfide and washing with water. The peptisation takes place with the aid of H_2S. The method does not always lead to successful results for the sulfides even more than the oxides have the tendency to form precipitates, and in this state they cannot be peptised. In this regard they have properties midway between the oxides on the one hand and the metals on the other. Their reactions are in general similar to those of the metals.

2. A second method is given by Winssinger. Very dilute solutions of metal salts are treated with H_2S. The concentration is so small that the amount of acid formed is not sufficient to cause coagulation.

3. The third method has been employed by Lottermoser § for the formation of concentrated solutions of colloidal sulfides. This ingenious method consists in the employment of such salts that the products with H_2S will not be highly dissociated. For instance, concentrated solutions of colloidal mercury sulfide were made by the use of mercury cyanide. The HCN formed is of course very weakly dissociated and therefore cannot have a great precipitating effect. He also prepared colloidal copper sulfide by means of copper glycocoll and H_2S.

The treatment of oxides by H_2S, by which no electrolyte is formed has already been spoken of in connection with the preparation of arsenious sulfide.

Schulze ¶ prepared antimonious sulfide by treating tartar emetic with H_2S, and also by conducting H_2S into a solution of antimonious oxide in tartaric acid. The hydrosol is orange red and can be obtained in such a fine state of subdivision that the solution is clear in either transmitted or reflected light. Colloidal cadmium sulfide was made by Prost || from a precipitate of cadmium sulfide, obtained by the action of H_2S on an ammoniacal solution of cadmium sulfate. The well-washed precipitate was suspended in water and then treated with a current of H_2S whereby the cadmium sulfide went into colloidal solution. The color was golden yellow and manifested a diffusion of light rays in reflected light.

* W. Spring et G. v. Boeck: Bulletin de la Soc. chim. (**2**), **48**, 165–170 (1887).

† C. Winssinger: *Ibid.* (**2**), **49**, 452–457 (1888).

‡ E. A. Schneider: Ber., **24**, 2241–2247 (1891).

§ A. Lottermoser: Journ. f. prakt. Chemie (**2**), **75**, 293–306 (1907).

¶ H. Schulze: Journ. f. prakt. Chemie (**2**), **27**, 320–332 (1883).

|| E. Prost: Bull. Acad. Roy. Belg. (**3**), **14**, 312–321 (1887).

CHAPTER IX

COLLOIDAL SALTS

JUST as in the case of difficultly soluble metals, sulfides, and oxides, almost all other insoluble bodies may be obtained in the colloidal form. Of importance are the colloidal salts, which may be prepared either as hydrosols or hydrogels. Graham * obtained colloidal copper ferrocyanide by dissolving the brown precipitate in ammonium oxalate, and subsequent dialysis. He also prepared colloidal Prussian blue by a similar method. Schneider † obtained a hydrosol of ferric phosphate, Lottermoser and E. v. Meyer ‡ colloidal silver halides, while Lottermoser ‡ has made a whole series of hydrosols of difficultly soluble salts. Recently the number of these hydrosols has been greatly increased by the work of von Weimarn.§

Colloidal Silver Halides. — Hydrosols of silver chloride, bromide, and iodide were prepared by Lottermoser and E. v. Meyer ¶ by treating colloidal silver with the corresponding halogen. They were very sensitive to electrolytes. Another theoretically interesting method has also been worked out by Lottermoser. || It is based on the effect of silver nitrate on the silver halides. By this method have been prepared colloidal solutions of silver chloride, bromide, iodide, cyanide, ferro and ferricyanides, phosphate and arsenate. The reaction is particularly interesting because it can be followed by measurement. It may be carried out in two ways. Either a measured amount of silver nitrate is treated with dilute solutions of the alkali halides, or silver nitrate from a buret is added to a known amount of the halide. In the first there must be an excess of the silver ion and in the second an excess of the halide ion in order to obtain a hydrosol. If too much of the lesser constituent is added precipitation results.

1. 25 cc. of a N/10 KBr are placed in a small flask and N/20 silver nitrate solution added from a buret with violent shaking. A hydrosol

* Th. Graham: Liebigs Annalen, **121,** 48 (1862).

† E. A. Schneider: Zeit. f. anorg. Chemie, **5,** 84–87 (1894).

‡ A. Lottermoser und E. v. Meyer: Journ. f. prakt. Chemie (**2**), **56,** 247 (1897). A. Lottermoser: *Ibid.* (**2**), **57,** 484–487 (1898); **68,** 341 (1903) u. a.

§ von Weimarn: Koll.-Zeit., **2–5.**

¶ *l. c.*

|| A. Lottermoser: Journ. f. prakt. Chemie (**2**), **72,** 39–56 (1905).

of silver bromide is formed having opalescent properties. Shortly before the bromide ion is completely converted into silver bromide the solution is turbid and not very stable. When about 50 cc. of the silver nitrate have been added a curdy precipitate comes out.

2. The second method is the opposite of the first; that is to say, the potassium bromide solution is in the buret and is added to the solution of silver nitrate. The phenomena are quite analogous, but the hydrosols differ in one important particular. In the first case as long as the halide ion is in excess of the silver, the ultramicrons are charged negatively, while in the second case where the silver ion is in excess the ultramicrons are charged positively. The two halide hydrosols mutually precipitate each other, as is to be expected from a mixture of oppositely charged colloids.

By the use of formulas such as we have employed on pages 75 to 81 this behavior of these hydrosols may be at once accounted for. In method 1 the KBr is in excess. According to the formula $Ag^+ + Br^- \rightarrow AgBr$ insoluble silver bromide is formed that remains in solution as ultramicrons. The negative charge is the result of the adsorption of bromide ion by these ultramicrons in a greater degree than the positive ions, such as the potassium, hydrogen ion, or silver ion. It is scarcely to be doubted that the bromide is responsible for the charge because coagulation takes place at once as soon as enough silver has been added to unite exactly with the adsorbed bromide ion. From this it does not follow that each particle of silver bromide adsorbs one bromide ion molecule. In fact it is probable that the ratio of particles to adsorbed ion molecules is much greater at the beginning of the reaction than it is at the end. In other words a silver bromide may adsorb relatively more bromide ion when the concentration of the bromide is greatest. Nevertheless for the purposes of illustration let us assume that the complex is represented by the formula $\boxed{AgBr}\,Br^-$. As the amount of silver and bromide become equivalent at the end of the titration the ultramicrons are discharged according to the following equation:

$$\boxed{AgBr}\,Br^- + Ag^+ \rightarrow \boxed{AgBr} - BrAg.$$

This presentation is by no means a complete description of the entire process, for in point of fact the liquid becomes more and more turbid, which would indicate that the ultramicrons are uniting among themselves to form larger colloidal complexes, and finally a flocculent precipitate. It is natural to suppose that the ultramicrons would grow during the titration because the solution is constantly being supersaturated with silver bromide formed by the addition of silver nitrate to the potassium bromide. The ultramicrons already present would doubt-

less act as nuclei for the formation of fresh silver bromide. Moreover where the silver is being added to the solution of potassium bromide there is always an excess of silver ion that would neutralize the ultramicrons in the vicinity and thus allow them to unite with one another. Further, some of the ultramicrons will become positively charged because of the excess of silver ion, and therefore the oppositely charged ultramicrons would neutralize one another and unite to form larger particles when the liquid is shaken. A microscopical investigation would give additional information about the question.

In the second method the silver ion is always in excess. From a similar form of argument we have the ultramicrons adsorbing the silver ion and therefore charged positively. As the bromide ion is added the charge is neutralized on the ultramicrons and coagulation takes place accompanied by processes already described in the preceding paragraph.

Stability of the Hydrosols of Silver Halides. — The hydrosols obtained by the above processes are not very stable; they coagulate on standing, sometimes with comparative rapidity. They are less stable than the colloidal metals. Because the precipitate has no appreciable electric charge the neutralization must have occurred immediately before or during the union of the particles. This neutralization must be caused by the giving up of the adsorbed ion molecules, or by the adsorption of oppositely charged ion molecules.

Colloidal Silver Iodide and Other Salts. — Lottermoser prepared hydrosols of silver iodide by the same method used for silver chloride and bromide. Silver iodide hydrosols when concentrated are very turbid and under the ultramicroscope the disperse phase appears in the form of rapidly moving bright particles. As early as 1902 the author * was able to show that these hydrosols could be obtained containing particles that are amicroscopic. The solutions are made by mixing very dilute silver nitrate and potassium iodide. These hydrosols are particularly suitable for observing the gradual change from amicroscopic to submicroscopic particles.

By a similar method Lottermoser was able to prepare hydrosols of silver ferro and ferricyanide, phosphate, and arsenate. In these instances it was found easier to prepare hydrosols by allowing silver nitrate to flow into the solution of the alkali salt in question than it was by the reverse process. These solutions differ in this respect from the hydrosols of silver halides. Similar conditions hold for the preparation of the hydrosols of copper or iron ferrocyanides.

Photohaloids. — Silver halides possess the well-known property of turning black, when exposed for a sufficient length of time to the action

* R. Zsigmondy: Zur Erkenntnis der Kolloide, 149 (1905).

of light. Of more importance, however, is the property of accelerated reduction by suitable reagents on short exposure to the light. On this principle depends the art of photography. The white plate that has been exposed contains the latent image and the substance of this latent image is a much disputed point in photography.

That bromine is liberated from silver bromide by the action of light is an undisputed fact. But whether the reduction forms silver or a subbromide is a matter of much discussion. By treating silver chloride with a suitable reducing agent Lea * obtained colored products that he named photohaloids, and which he regarded as combinations of silver chloride with a subchloride. These substances corresponded in many ways with the products of light on silver chloride and silver bromide, hence these were included under the name photohaloids. Baur † demonstrated that photohaloids could be made by treating colloidal silver with the halogens. He also assumed the existence of subhalides. Abegg ‡ has shown, however, that in order to explain the properties of light exposed silver salts it is merely necessary to assume that a portion of the salt is reduced to silver. The assumption of a subhalide is therefore superfluous. On the other hand several authors, notably Eder,§ have defended the subhalide theory. This theory has received some support from the work of Güntz ¶ on silver subfluoride, and also from some electrochemical investigations of Luther.||

The question is to be divided into two others. First, do subchloride bromides and iodides of silver exist? This question is justified because the only subhalide of which we are sure is Ag_2Fl, made by Güntz, and later by L. Wöhler and Rodewald.** For the existence of other subhalides the best evidence we have is the experiments of Luther, which have received some discredit from the researches of Heyer,†† and Weisz.‡‡

The second question that presents itself is, what is the necessity of assuming the existence of a subhalide in the latent image or in the photohaloids? This question must be answered in the negative. The

* M. Carey Lea: Kolloides Silber und die Photohaloide. German ed. by Lüppo-Cramer. Dresden (1908).

† E. Bauer: Zeit. f. phys. Chemie, **45**, 613–626 (1903).

‡ R. Abegg: Wiedemanns Annalen d. Physik, N. F., **62**, 428 (1897); Archiv. f. wiss. Photographie, **1**, 15 ff. (1900).

§ M. Eder: Photogr. Korresp., 276, 332, 463, 650 (1899); Photogr. Jahrbuch, 80–87 (1900); Sitzungsber. d. Akad. d. Wiss. Wien, **114**, IIa, 1159–1193 (1905).

¶ Güntz: Compt. rend., 110, 1337–1339 (1890).

|| R. Luther: Zeit. f. phys. Chemie, **30**, 628–680 (1899).

** L. Wöhler und G. Rodewald: Zeit. f. anorg. Chemie, **61**, 54–90 (1909).

†† F. Heyer: Inaug.-Diss. Leipzig (1902).

‡‡ H. Weisz: Zeit. f. phys. Chemie, **54**, 305–352 (1906).

advocates of the subhalide theory contend that if the photohaloids were simply mixtures of silver and the silver salt the silver could be dissolved out by nitric acid. On the basis of investigations with pyrosols, ruby glass, and colloidal solutions R. Lorenz* has shown that the subhalide hypothesis is unnecessary. Lüppo-Cramer† has recently investigated the objection to the assumption that the photohaloid is a mixture of silver and silver halide, and has come to the conclusion that the objection is not well founded. Lüppo-Cramer‡ has succeeded in demonstrating that silver bromide may protect colloidal silver from the attack of nitric acid. If the hydrosols of silver and silver bromide are mixed and concentrated nitric acid immediately added, the colloidal silver will be dissolved. If, however, the mixture is first coagulated by sulfuric acid, a colored photohaloid is obtained from which the silver cannot be extracted by nitric acid. Likewise the same author has shown that colloidal gold cannot be dissolved by aqua regia if the gold is first precipitated simultaneously with silver bromide. It should be further remarked with regard to the idea of removing the silver from the mixture by nitric acid, that the properties of colloidal mixtures differ widely from those of the several constituents individually, and often resemble chemical combinations. This was exemplified very well in the case of the purple of Cassius. Furthermore, it has been shown that metastannic acid, copper oxides, and many others cannot be extracted by nitric acid. As far as the color of the photohaloids are concerned it should be remembered that it corresponds to that of colloidal silver, even when mixed with the silver halides.

One could form a rough picture of the protective process by assuming that the particles are surrounded by the silver bromide and thus the nitric acid could not reach the silver. It is probable that the process is much more complicated than this, and that its true nature is not yet understood.

It is interesting that gold nuclei can cause the reduction of silver in a colloidal silver bromide mixture, just as they can in a suitable homogeneous solution of silver salt and reducing agent. Such observations have been made by Weisz§ and also in the author's laboratory by Thomæ. For this purpose a gold nuclear solution is employed with a hydrosol of silver bromide prepared and dialyzed in the dark. The hydrosol is put into two small vessels to one of which is added the gold

* R. Lorenz: Elektrolyse geschmolzener Salze, 2, 69 ff. Halle (1905).

† Lüppo-Cramer: Mitteilungen in der Photogr. Korrespondenz, Koll.-Zeit. und Monographien: Photographische Probleme, 117. Halle (1907); Kolloidchemie und Photographie, 70. Dresden (1908). Das latente Bild, Halle (1911).

‡ Lüppo-Cramer: Photogr. Korr., 289 (1907); 397, 415, 526 (1909).

§ *Ibid.*, 328.

nuclear solution. Both solutions are now precipitated with an indifferent electrolyte, such as potassium bromide. If now a suitable developer is added to both vessels, a darkening in color will begin almost immediately in the one containing the nuclear solution, while the other will remain for a long time without any change. Naturally all these operations must take place in the dark room. The nuclear solution has had the same effect as exposure to light. Nuclear solutions of silver have the same property. From this it follows that it is merely necessary to have nuclei present in order to account for the development of the image on a photographic plate by the developing solution, and the photohaloids can therefore be regarded as mixtures of silver and silver halide.*

To account for all the properties of the latent image much more complicated assumptions are necessary. These cannot be taken up here, but it is quite possible that a colloidal point of view may be employed for the explanation of solarization and other little understood phenomena. The author would like to call attention to a not widely known experiment of Kogelmann,† by which it is shown that with normally exposed plates developed in acid solution containing iron, the substance of the latent image lies on the surface of the granules, while this substance is in the granules in the case of solarized plates.

Colloidal Ferrocyanides. — The most simple method for the preparation of colloidal ferrocyanides is to pour a dilute solution of the metal in question into a solution of potassium ferrocyanide. Graham's method,‡ which is to dissolve the precipitated cyanide in ammonium oxalate, is of little interest. The hydrosols show in general the same color as the hydrogels obtained from them. They are sometimes quite homogeneous, sometimes filled with ultramicrons that are in rapid motion.

Colloidal copper ferrocyanide can be made by pouring a dilute solution of copper chloride into a dilute solution of potassium ferrocyanide. The hydrosol thus formed is clear and has a reddish brown color. With increasing concentration of copper the solution becomes more and more turbid and finally such concentration relations are obtained that the hydrosol coagulates. This relation between the concentrations is not what one would predict from a knowledge of the equivalents of the cupric and ferrocyanide ions, but as shown by Duclaux§ coagulation

* K. Sichling: Zeit. f. phys. Chemie, **77**, 1–57 (1911). W. Reinders: Zeit. f. phys. Chemie, **77**, 213–226 (1911).

† F. Kogelmann: Die Isolierung der Substanz des photographischen Bildes. Graz (1894).

‡ Th. Graham: Liebigs Annalen, **121**, 48 (1862).

§ J. Duclaux: Journ. de Chim. Phys., **5**, 29–56 (1907).

takes place long before enough copper has been added to unite exactly with the cyanide. The concentration relations just before coagulation occurs have been called by Duclaux the "point critique." A small excess of copper over this relation causes complete precipitation, while a similar excess of ferrocyanide insures the stability of the hydrosol.

The precipitate contains according to Duclaux some potassium even in the presence of an excess of copper, and the formula is

$$(FeCy_6)\ Cu_mK_n$$

where $m + \frac{n}{2} = 2$. By the precipitation with an excess of copper chloride n varies between 1.3 and 0.2. At the critical point where the coagulation first begins the formula for the precipitate is approximately

$$(FeCy)\ Cu_{1.9}K_{0.2}.$$

Thus it is seen that the cupric ferrocyanide carries down a part of the potassium ferrocyanide, and that the latter cannot diffuse into the surrounding liquid nor send off ion molecules because of dissociation. Duclaux believes this potassium ferrocyanide is chemically combined. This property is probably connected with the power of copper ferrocyanide to form semipermeable membranes for crystalloids.

When the potassium ferrocyanide is in excess a hydrosol is always formed the particles of which are charged negatively. From this we must conclude that the ferrocyanide ion is adsorbed. When sufficient cupric ion has been added to unite exactly with the adsorbed cyanide, coagulation results. The reaction may be expressed by the following equation:

$$\boxed{\begin{matrix} Cu_2FeCy_6 \\ K_2FeCy_6 \end{matrix}}\ FeCy_6^{=\,=} + 2\,Cu^{++} \rightarrow \boxed{\begin{matrix} Cu_2FeCy_6 \\ K_2FeCy_6 \end{matrix}}\ FeCy_6Cu_2.$$

For the cupric ion any other ion in equivalent amount may be substituted to cause the precipitation. This tendency of the colloid to adsorb the potassium ferrocyanide is important in analytical chemistry. It is evident that potassium ferrocyanide cannot be titrated with cupric chloride because the end point will be reached before an equivalent amount of cupric ion has been added. A great many other precipitates behave similarly and herein lies the reason that zinc salts cannot be titrated accurately with potassium ferrocyanide or sodium sulfide.

Other Colloidal Salts

It is well known that the hydrosols of many different substances may be prepared in dilute solution by means of chemical reactions in a medium in which the colloid is insoluble. This is the method followed

in the preparation of hydrosols of most salts. In the case of the more soluble salts the medium must be chosen so that the solubility will be as greatly decreased as possible. For instance the solubility of barium sulfate is too great to allow the preparation of the hydrosol without the presence of a protective colloid.* Neuberg † prepared a hydrosol of barium carbonate by conducting a current of CO_2 into a solution of barium oxide in methyl alcohol. The gel at first formed dissolves spontaneously on standing in methyl alcohol. In a similar manner the gels of barium sulfate, calcium, and magnesium carbonate have been made.‡ With regard to the preparation of organosols of easily soluble salts Paal § and his collaborators have given many examples.

Colloidal Sodium Chloride. — According to Michael ¶ chloracetic ester and sodium malonic ester react to form a weakly opalescent liquid. He considers the following reaction probable,

$$ClCH_2CO_2C_2H_5 + CHNa\begin{matrix} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{matrix} \rightarrow C_{11}H_{18}O_6ClNa$$

whereby an addition product of ethenyltricarbonic ester is formed. Paal has shown however that ethenyltricarbonic ester and sodium chloride are formed by the interaction of the above two substances. The clearness of the solution is due to the sodium chloride remaining in solution as a colloid. The substance with the high molecular weight acts as a protective colloid for the colloidal sodium chloride. Petroleum ether will precipitate the colloid, but it dissolves again with unchanged properties in benzol. In a similar manner Paal and Kühn have prepared organosols of sodium bromide and sodium iodide. The employment of protective colloids is a general device for the preparation of hydrosols. Lobry de Bruyn || made use of gelatin in the preparation of not only colloidal metals, but also a series of salts such as colloidal silver chloride, silver chromate, etc. Paal and Voss ** prepared hydrosols of many salts,

* R. Zsigmondy: Zur Erkenntnis der Kolloide, 150 (1905).

† C. Neuberg und E. Neimann: Biochem. Zeit., **1**, 166–176 (1906). Ders und B. Rewald: Koll.-Zeit. **2**, 321–324 (1908).

‡ C. Neuberg: Sitzungsber. d. Akad. d. Wiss., 820–822. Berlin (1907).

§ C. Paal: Ber., **39**, 1436–1441 (1906). Ders. und G. Kühn: Ber., **39**, 2859–2866 (1906); **41**, 51–61 (1907). Ders. und K. Zahn: Ber., **42**, 277–300 (1909).

¶ A. Michael: Ber., **38**, 3217–3234 (1905).

|| C. A. Lobry de Bruyn: Receuil d. travaux chim. des Pays-Bas, **19**, 236–249 (1900).

** C. Paal und F. Voss: Ber., **37**, 3862–3881 (1904).

among others silver phosphate and silver carbonate, in the presence of the sodium salt of prot- or lysalbinnic acid. Several patents have been taken out for the preparation of such colloids. For instance the chemical works of Heyden in Radebeul have a patent for the preparation of mercurous halides and silver chromate soluble in water. Other patents are held by Kalle & Co.

Hydrogels of Difficultly Soluble Salts. — It is remarkable that difficultly soluble salts separate out in the form of a gel if made in very concentrated solution. These phenomena have been noticed by Harting,* Buchner,† Biedermann ‡ and Neuberg,§ and especially studied by Weimarn.¶ As an example of this may be cited barium sulfate jelly that may be obtained by mixing concentrated solutions of sulfocyanate and manganous sulfate. This gel gradually turns into a crystalline powder, and the change from colloidal particles to tiny crystals has been followed under the ultramicroscope by Weimarn. If more dilute solutions of barium sulfocyanate and manganous sulfate are mixed a granular precipitate is formed directly.

* P. Harting: Recherches de morphologie synthétique sur la production artificielle de quelques formations calcaires organiques. Amsterdam (1872).

† G. Buchner: Chem.-Ztg., **17**, 878 (1893).

‡ W. Biedermann: Zeit. f. allg. Physiol., **1**, 154–208 (1902).

§ *l. c.*

¶ P. P. v. Weimarn: Koll.-Zeit. Bd., **2–5**, in Mitteilungen "Zur Lehre von den Zuständen der Materie."

CHAPTER X

ORGANIC COLLOIDS *

Colloidal Organic Salts

Colloidal organic salts, important both in technical and colloidal chemistry, may be conveniently divided into two classes, soaps and dyestuffs. The two classes have much in common, nevertheless they exhibit great differences.

Soaps

Under soaps we will understand the salts of the higher fatty acids and resins with acid properties. The first named have been subjected to elaborate investigation by Krafft † and his students.

Raising of the Boiling Point. — The alkali salts of fatty acids with low molecular weight such as formic, acetic, and propionic acids are dissociated in aqueous solution in a normal manner, and are of no great interest for the present work. On the other hand the salts of the higher acids, such as palmitic, stearic, lauric, myristic, and oleic, possess individual properties of an extraordinary nature. In alcohol they behave as ordinary crystalloids; that is they crystallize out on evaporation, and raise the boiling point corresponding to a normal molecular weight. In concentrated aqueous solution, on the contrary, they are colloids; that is they do not raise the boiling point, become gels on cooling, may be salted out, and do not diffuse through membranes, or at least very slowly. We have here well-defined chemical substances that are either crystalloids or colloids according to the solvent employed. Salts of fatty acids lying between these two extremes have properties partly colloidal and partly crystalloidal. This can be seen from Table 28.

A somewhat greater concentration of capronate gives no raising of the boiling point and the solution gels on cooling. The nonylate shows an appreciable raising of the boiling point that becomes relatively less and less as the concentration increases. The salts of the higher fatty acids show no raising.

* Chapters X, XI, XII.

† F. Krafft und A. Stern: Ber., **27**, 1747–1761 (1894). Ders. und H. Wiglow: Ber., **28**, 2566–2582 (1895). Ders. und A. Strutz: Ber., **29**, 1328–1334 (1896). Ders.: Ber. **29**, 1334–1344 (1896).

TABLE 28

Substance.	Formula.	Gms. in 100 gms. water.	Molecular weight calculated from		
			a Boiling point.	b Mol. wt. of acid.	$\frac{a}{b}$
Sodium acetate.........	$NaC_2H_3O_2$	0.9 25.2	50.5 40.3	82	0.6 0.5
Sodium propionate......	$NaC_3H_5O_2$	3.8 19.8	51.7 46.2	96	0.6 0.5
Sodium capronate.......	$NaC_6H_{11}O_2$	3.5 20.6 31.9 95.9	72.8 77.9 84.4 98.5	138	0.52 0.56 0.61 0.71
Sodium nonylate........	$NaC_9H_{17}O_2$	3.4 20.4	144.1 285.5	180	0.8 1.58
Sodium palmitate.......	$NaC_{16}H_{31}O_2$	16.4 25	ca. 1060 Nearly infinite	278	ca. 4 Nearly infinite
Sodium stearate........	$NaC_{18}H_{35}O_2$	16 27	ca. 1500 Nearly infinite	306	ca. 5 Nearly infinite
Sodium oleate..........	$NaC_{18}H_{33}O_2$	26.5	Nearly infinite	304	Nearly infinite

Kahlenberg and Schreiner * sought to explain this remarkable fact by the assumption that the solutions of soap do not boil normally. Careful and elaborate experiments of Krafft † have shown that the standpoint of Kahlenberg and Schreiner is not well taken, and that solutions of soap do boil normally. In six soap solutions, where the most concentrated did not of themselves raise the boiling point, electrolytes such as sodium chloride gave the same rise as they do in pure water. Krafft also showed that the alcoholic solution of sodium oleate gave a normal rise as seen in the following table.

TABLE 29

Gms. alcohol.	Gms. sodium oleate.	Rise in b.p.	Mol. wt. (calculated = 304.4)
14.7	0.5045	0.131	301.3
14.7	1.2073	0.273	345.9
14.7	1.9925	....	Incompletely dissolved

Moreover Krafft ‡ found a most extraordinary regularity in the gelatinization of soap solutions, the temperature being almost identical

* L. Kahlenberg und O. Schreiner: Zeit. f. phys. Chemie, **27**, 552–566 (1898).
† F. Krafft: Ber., **32**, 1584–1596 (1899).
‡ *Ibid.*, 1596–1608 (1899).

with the melting point of the pure acids, as seen in Table 30. From this he concludes that these salts must be partly hydrolyzed. This is substantiated by the fact that the fatty acid may be extracted by certain solvents, such as toluol, from concentrated soap solutions. Further evidence is afforded by the behavior during dialysis. The largest portion of that diffusing through is alkali while the acid remains on the membrane. This hypothesis does not explain the want of any rise in the boiling point. If any free alkali is present the effect on the boiling point should be evident. In a recent and thorough investigation by J. W. McBain and M. Taylor * the assumption of Krafft has been corroborated. They explain the absence of any rise in the boiling point by the presence of air in the soap solution, the partial pressure of which is added to that of the water and thus causes a lowering in the boiling temperature. By means of conductivity measurements they were able to show the existence of an equilibrium between electrolyte, colloid, and coagulum. They also submit evidence which goes to show that the equilibrium may be expressed by the equation:

TABLE 30

Sodium stearate	$C_{18}H_{35}O_2Na$	Melting point ca. 260°
Stearic acid	$C_{18}H_{36}O_2$	" " " 69.4°
Concentration of solution	....	20% 15% 10% 1%
Solidification temperature	....	69° 68° 68–67° 60°
Sodium palmitate	$C_{16}H_{31}O_2Na$	Melting point about 270°
Palmitic acid	$C_{16}H_{32}O_2$	" " " 62°
Concentration of solution	....	20% 1%
Solidification temperature	....	62–61.8° 45°
Sodium myristate	$C_{14}H_{27}O_2Na$	Melting point ca. 250°
Myristic acid	$C_{14}H_{28}O_2$	" " " 53.8°
Concentration of solution	....	20% 1%
Solidification temperature	....	53–52° 31.5°
Sodium laurate	$C_{12}H_{23}O_2Na$	Melting point ca. 255–260°
Lauric acid	$C_{12}H_{24}O_2$	" " " 43.6°
Concentration of solution	....	25% 20% 1%
Solidification temperature	....	45–42° ca. 36° ca. 11°
Sodium oleate	$C_{18}H_{33}O_2$	Melting point ca. 232–235°
Oleic acid	$C_{18}H_{34}O_2$	" " " 14°
Concentration of solution	....	25% 1%
Solidification temperature	....	13–6° 0°
Sodium elaidate	$C_{18}H_{33}O_2Na$	Melting point 225–227°
Elaidic acid	$C_{18}H_{34}O_2$.	" " 45°
Concentration of solution	....	20% 1%
Solidification temperature	....	45.5–44.8° 35°

$$\text{Soap} + H_2O \rightleftarrows \text{Acid sodium salt} + NaOH.$$

That is to say it is not the acid that is set free by hydrolysis but an acid salt. According to F. G. Donnan and A. S. White no well-defined chemical compounds are formed by melting a mixture of sodium palmi-

* J. W. McBain and M. Taylor: Zeit. f. phys. Chemie, 76, 179–209 (1911).

tate and palmitic acid.* If McBain's assumption with regard to the air does not hold quantitatively we are obliged to believe that the alkali is completely adsorbed by the colloidal particles of the acid salt, free acid if present, and by the unhydrolyzed soap. That adsorption does take place, and that sodium hydroxide and its chemical combinations emulsify the higher fatty acids has been shown by Donnan.†

Osmotic pressure measurements give just as abnormally high molecular weights as the boiling point. For sodium oleate Moore and Parker ‡ obtained the results given in Table 31.

TABLE 31

Concentration, per cent.	$T°$.	Mol. wt.
0.5	55	7,100
3.0	40	15,700

Conductivity measurements by Kahlenberg and Schreiner § on dilute soap solutions show complete hydrolysis and the formation of an insoluble acid salt. This agrees with the researches of McBain.

The colloidal nature of soap solutions is manifested by the protective action on gold solutions. The gold number of sodium oleate lies between 0.5 and 2. The protective effect is therefore about as great as that of gum arabic, and much smaller than that of gelatin. The protective effect of sodium stearate increases with the temperature.

Detergent Effect of Soap

Regarding the detergent effect of soaps Spring ¶ has carried out some interesting experiments. The older theories of Chevreul,|| Falck,** etc., attributed the detergent effect to the hydrolysis of the soap, or to the power to distend the fats, and also to the emulsifying effect. Spring has demonstrated another effect of the soap. There are a great many substances free from fats that stick fast to another surface also free from fats. These substances cannot be washed off by pure water, but if soap be added they come away easily. Examples are MnO_2,

* F. G. Donnan und A. S. White: Journ. Chem. Soc., **99**, 1668–1679 (1911).

† F. G. Donnan: Zeit. f. phys. Chemie, **31**, 42–49 (1899).

‡ B. Moore and W. H. Parker: Amer. Journ. of Physiol., **7**, 261 (1902).

§ *l. c.*

¶ W. Spring: Koll.-Zeit., **4**, 161–168 (1909); **6**, 11–17, 109–111, 164–168 (1910).

|| M. Chevreul: Recherches chimique sur les corps gras d'origine animale. Paris (1910).

** R. Flack: Archiv. f. klin. Chirurg, **73**, 405–437 (1904). Zeit. f. Elektrochemie, 10, 834 (1904).

Fe_2O_3, animal charcoal, etc. This property on the part of the soap is closely allied to the tendency to lower the surface tension. The soap piles up on the surface of the particles of the matèrial that clings and prevents it from adhering to the surface in question.

Spring washed pine soot with alcohol, ether, benzol, and finally with benzol vapors in order to free the soot of grease. Soot differs in its properties after this treatment in that it will form a stable suspension in water. It can be filtered out with filter paper however. If the soot is mixed with a 1 per cent solution of soap it passes through the filter paper, not even so much as staining it. The soot is therefore not strained out by the paper but is adsorbed on the surface. If the filter containing the soot is turned inside out and water passed through, the soot remains on the paper. Soap solution will remove it quite easily. Spring has also shown that the soap is adsorbed by many other substances beside soot, and that this concentrating of the soap on the surface is the chief factor in the detergent action. It seems probable that in addition to the adsorption a reaction analogous to peptisation, that is a charging of the fibers and the particles of soot by ion adsorption, takes place.

Interesting also is the corroboration by Spring of some observations by Donnan and Potts,* that the stability of soot suspensions in soap solutions goes through a maximum as the concentration of the soap increases. This maximum is situated at about 1 per cent. At 2 per cent the soot sinks to the bottom almost as fast as in pure water.

Emulsification of the Fatty Series

Investigations on the emulsifying effect of the sodium salts of high-fatty acids on the members of the fatty series have been carried out by Donnan.† He hàs demonstrated that the surface tension between water and fats is reduced by the presence of soap. This reduction is appreciable from the sodium salt of caprylic acid upwards in the series. It is also noteworthy that according to the observations of Krafft, and the ultramicroscopic investigations of Mayer, Schaeffer, and Terroine,‡ the colloidal character of these salts begins to be pronounced with caprylic or lauric acid. Later experiments have shown that the emulsifying effect also begins to be appreciable with laurates and myristates. This effect goes through a maximum in the case of laurates as the concentration increases.

* F. G. Donnan und H. E. Potts: Koll.-Zeit., **7**, 208–214 (1910).

† F. G. Donnan: Zeit. f. phys. Chemie, **31**, 42–49 (1899).

‡ A. Mayer, G. Schaeffer et E. F. Terroine: Compt. rend., **146**, 484–487 (1908).

CHAPTER XI

DYESTUFFS

SIMILAR to the soaps many dyestuffs are salts of more or less basic or acid properties, and possess a colloidal nature. They are often hydrolyzed and have colloidal tendencies because of this. However in cases where hydrolysis plays no important part the colloidal character is often quite pronounced, for instance in the alkali salts of the sulfo-acids. In general, those with high molecular weights tend to go into the colloidal state.* Many of them do not, or at least very slowly, diffuse through membranes, and may be precipitated by colloids having an opposite charge. According to the character of the charge they migrate in a potential fall either to the cathode or to the anode, as was first shown by the researches of Picton and Linder.†

Perhaps the most convincing evidence of the colloidal nature of dyestuffs is given by the ultramicroscopic observations of Raehlmann, Michaelis, Höber, and others. These investigators have demonstrated that solutions of dyestuffs are sometimes filled with ultramicrons even when the liquid becomes colorless because of the great dilution. In confirmation of this view are the experiments of Krafft ‡ which show that many of these salts such as Methyl Violet raise the boiling point of water correspondingly less than that of alcohol.

Most of the work done on dyestuffs has been concerned with practical applications in the textile industry, or with the staining of living cells in microscopical observations. The preparations used were those obtainable on the market and were rarely pure chemical substances. This disregard for strictly scientific principles has led to the accumulation of a lot of contradictory results. On the other hand it should be considered that these investigations were for practical purposes, and it is precisely with these impure technical preparations that the industries have to do. These investigations have their value in technical life but before we can know the truth, careful work must be done with pure substances. A good start in this direction has been

* W. Biltz: van Bemmelen-Gedenkboek, 108–120 (1910).

† H. Picton and S. E. Linder: Journ. Chem. Soc., **71**, 568–573 (1897).

‡ F. Krafft: Ber., **32**, 1608–1622 (1899).

made by Knecht, Bayliss, Biltz and v. Vegesack. Work on the dyestuffs may be conveniently divided into three classes:

1. Those which have to do with the state of the dyestuff, ultramicroscopy, diffusion, dialysis, precipitation with electrolytes, osmotic pressure, and with the conductivity.

2. Those concerned with the reactions of dyestuffs toward one another, with other electrolytes, and with positively or negatively charged inorganic colloids.

3. Those which have to do with technical dyeing, coloring or staining of cells or bacteria.

Ultramicroscopy and Dialysis of Dyestuffs. — After Raehlmann * had shown that solutions of dyestuffs were often filled with ultramicroscopical particles, L. Michaelis † undertook an elabroate investigation and endeavored to divide the solutions according to the appearance in the ultramicroscope. His classification is as follows:

1. Those completely resolvable under the ultramicroscope. To those belong the salts of sulfoacids with high molecular weights, such as Aniline Blue, water soluble Induline, Bayrisch Blue, Violet Black; in addition, certain pseudo solutions such as Fuchsine in aniline water, Fuchsine in sodium chloride (prepared hot, turbid when cold turning violet to blue); also the product which is obtained when alcoholic solutions of Scharlack are poured into water.

2. The partially resolvable. Those containing the dissolved substance in two phases; the optically void, and those in the form of ultramicrons. To this class belong concentrated aqueous solutions of Fuchsine, Methyl Violet, Neutral Red, Capri Blue, etc.

3. Those not resolvable, as Fluorescein, Eosine, Nile Blue, Methylene *Blue, Magdala Red, etc.*

Among other things Michaelis found that class 1 had the property of dyeing all sorts of fibers, while the third class stained living cells particularly well. This was confirmed by Höber and F. Kempner, ‡ who were engaged in the adsorption of dyes by the cells in the kidneys of frogs. In their investigations they used only "lipoidunlosliche." They found, in agreement with the researches of Michaelis and Raehlmann that a part of the dissolved substance was in the form of ultramicrons. Indeed solutions of dyestuffs enumerated in class 1 were filled with ultramicroscopical particles, even at great dilutions, while other dyestuffs contained scarcely any.

* E. Raehlmann: Physikal. Zeit., **4**, 884–890 (1903).

† L. Michaelis: Deutsche med. Wochenschr., 1534 (1904); Virchows Archiv, **179**, 195–208 (1905).

‡ R. Höber und F. Kempner: Biochem. Zeit., **11**, 105–120 (1908).

The results on diffusibility agree with those obtained by the ultramicroscope. The following column is arranged in the order of increasing diffusibility.

Prussian Blue, Congo Red, Alkali Blue, 3 B.
Bavarian Blue, Aniline Blue.
Violet Black.
Nigrosine.
Induline.
Aniline Orange, Indigo Carmine.
Acid Fuchsine.

A similar series was obtained from the results of precipitation with $CaCl_2$ and $NiCl_2$.

Teague and Buxton * have worked with the diffusibility through parchment membranes. They distinguish between strongly colloidal, medium, and weakly colloidal dyestuffs. They have arranged some basic and acid dyes in the following ascending order of diffusibility: Night Blue, Janus Green, Nile Blue, Neutral Red, Methylene Blue.

Acid dyestuffs: Congo Red, Trypan Red, Nigrosine, Biebrich Scarlet, Eosine, Alizarine Red.

An elaborate investigation by Raehlmann † was concerned with the ultramicroscopical behavior of a large number of natural and artificial colored substances, and some of their reactions. According to this work Alkali Blue, Benzoblue Black, Congo True Blue, water-soluble Chlorophyll, and colloidal Indigo belong to class 1. As in the case of the metals the color of the ultramicrons is complementary to that of the solution in transmitted light. The same author studied the reactions of different dyestuffs on one another, and observed in many cases a group-like assembling of the submicroscopical particles. He further observed that on being mixed with solutions of egg albumin the dyestuff particles united with those of the albumin to form flocks. It is therefore possible in the case of some organic colloids to follow certain reactions under the ultramicroscope that are of great importance in colloidal chemistry. It is also worthy of note that Raehlmann was not able, by the ordinary microscope and transmitted light, to detect the flocks formed, even when the size of the flocks attained 10 μ.

Composition and Colloidal Character of the Dyestuffs. — If one seeks the cause of the dialysis and the colloidal character of the dyestuffs, the influence of the size of the molecule is at once appar-

* O. Teague und B. H. Buxton: Zeit. f. phys. Chemie, **60**, 469–488, 489–506 (1907); **62**, 287–307 (1908).

† E. Raehlmann: Archiv. f. d. ges. Physiol., **112**, 128–171 (1906).

ent. From the results of F. Pfennigg, Biltz * has shown with about 150 dyestuffs that the number of atoms rather than the molecular weight is the important factor in the diffusibility through membranes. He defines the "Molekülgrösse" (size of the molecule) according to the number of atoms, and finds that those dyes containing up to 45 atoms diffuse quickly, those with 55 to 70 diffuse slowly, and those containing more than 70 do not diffuse at all. Certain constitutional influences override the effect of the number of atoms. Especially is this true of the sulfo group, the presence of which increases the solubility in water and the diffusibility. Dyestuffs containing from 70 to 95 atoms ought not to diffuse through parchment paper, but will quite easily if they contain a sufficient number of sulfo groups. For instance Alkali Blue 6 B with 76 atoms and one sulfo group does not diffuse, while True Acid Violet 10 B with 78 atoms and two sulfo groups passes through membranes comparatively easily. The Alizarine group on the other hand retards diffusion. Some alizarine dyestuffs with only 38 atoms do not diffuse.

Bredig † has found similar laws to hold for the rate of migration of organic electrolytes. The rate falls off rapidly with increasing number of atoms, then more slowly, and is greatly increased by the presence of the sulfo group.

Osmotic Pressure and Conductivity of Pure Dyestuff Solutions

Dyestuffs exist that have no power to diffuse through parchment membranes, and still as pure substances in solution, according to conductivity and osmotic pressure measurements, behave as electrolytes. To these belong salts of type of Congo Red, Night Blue. Ultramicroscopically they contain, according to conditions of concentration and presence of foreign electrolytes, amicrons or submicrons. In a pure state and at great dilution they may appear optically void. Knecht ‡ first drew attention to the fact that dyestuffs in a high state of purity, regarded as colloids because of their behavior toward parchment membranes, show a normal conductivity and raising of the boiling point. The osmotic pressure of a pure Congo Red solution against water, according to Bayliss, § is about that which would be calculated from its molecular weight. By the boiling-point method Knecht found 370 to

* W. Biltz: van Bemmelen-Gedenkboek, 108–120 (1910).

† G. Bredig: Zeit. f. phys. Chemie, **13**, 191–288 (1894).

‡ E. Knecht and J. Batey: Journ. Soc. of Dyers and Colourists, 25, No. 7 (July, 1909).

§ W. M. Bayliss: Proc. Roy. Soc., **91**, 269–286 (1909); Koll.-Zeit., **6**, 23–32 (1910).

412 for the molecular weight of Benzopurpurin instead of the formula weight 756.

In order to free Congo Red from foreign electrolytes Bayliss * precipitated it with HCl and dialyzed in a parchment osmometer until free from electrolytes. In this manner he obtained a blue colloidal solution of the free acid that showed a very small rise in the osmometer. To get the sodium salt he dialyzed against a solution of sodium hydroxide, which caused an extraordinary rise in the osmometer. The excess of alkali was removed by distilled water. After a week of dialysis the column retained a constant height of 50 mm. When the ordinary distilled water was replaced by conductivity water free from CO_2 there was a further rise in the osmometer, and the column remained at 97 per cent of what it should from calculation. Only a faint cloud was to be seen in the ultramicroscope. The extraordinary sensitiveness to carbonic acid, as revealed by the last experiment, has also been observed by Biltz and v. Vegesack.† In these experiments membrane hydrolysis must be considered, which, according to Donnan, plays a part even in the case of strong electrolytes.

Bayliss endeavored to determine the osmotic pressure of a series of dyestuffs that diffuse through membranes so that no constant pressure could be obtained in the osmometer. Aniline Blue with a molecular weight of 734 does not diffuse and shows only one-half the theoretical pressure. At the end of the experiment the ultramicroscope reveals a large number of bright submicrons in the diffused cone caused by the amicrons. Bayliss believes the solution consists of single molecules and some that have united to form submicrons. Endeavors to determine whether or not the osmotic pressure corresponded to the number of particles were not successful.

An elaborate investigation of the osmotic pressure of Benzopurpurin, Night Blue, and Congo Red was undertaken by Biltz and v. Vegesack. They substantiated the results of Bayliss that the osmotic pressure of pure Congo Red against water is smaller than that calculated from the formula weight. They also showed that the pressure was considerably less when dilute solutions of electrolytes were employed instead of pure water.

Influence of Electrolytes. — Dyestuffs of the Congo Red type are extraordinarily sensitive toward electrolytes. As shown by Bayliss mere traces of electrolytes are sufficient to coagulate the particles and

* W. M. Bayliss: Proc. Roy. Soc., **81**, 269–286 (1909); Koll.-Zeit., **6**, 23–32 (1910).

† W. Biltz und A. v. Vegesack: Zeit. f. phys. Chemie, **68**, 357–382 (1909); **73**, 481–512 (1910).

materially change the character of the solution. We have here examples of undoubted electrolytes that are just as sensitive toward salts as colloidal solutions of the metals.

Just as in the case of carbonic acid neutral salts also decrease the osmotic pressure. A $\frac{N}{\cdot 10}$ sodium chloride solution caused a fall of 207 to 15 mm., and when the sodium chloride was removed by dialysis the pressure did not go back to its former value. Traces of the alkali salts are sufficient therefore to reduce the number of particles to a fraction of the former amount.*

Biltz and v. Vegesack have looked into this matter also and have shown in the case of Benzopurple that the raising of conductivity of the outer water from 566.10^{-6} to 786.10^{-6} by the addition of salt was sufficient to reduce the osmotic pressure to one-half the original value, and to double the calculated average molecular weight. The former solution showed only a few particles and a faint light cone, while after the electrolyte had been added the solution manifested a pronounced light cone and about 200 particles.

Influence of Time. — As has been already stated several times hydrosols change their properties with the time. Dyestuffs are particularly suitable for demonstrating this phenomenon. Biltz and v. Vegesack made solutions, allowed them to age and at definite intervals measured the conductivity and the osmotic pressure. The latter decreased with the time, and the ultramicroscopic investigations showed an increase in the optical inhomogeneity. Concentrated solutions aged much more quickly than the more dilute. This phenomenon has been observed in other cases. The ageing may also be demonstrated by measuring the inner friction. The viscosity increases with the time.

Colloidal Precipitation of Dyestuffs. — The general laws governing the mutual precipitation of colloids have been discussed in Chapter III. Teague and Buxton † have contributed a not unimportant addition to the general results of Biltz,‡ Bechhold,§ Neisser and Freidemann.¶ The first two named investigated the mutual precipitation of dyestuffs and also the effect of certain organic colloids on both basic and acid dyestuffs. In general the law of precipitation holds here, that oppositely charged colloids precipitate each other if mixed in the

* J. G. Donnan and A. B. Harris: Journ. Chem. Soc., **99**, 1554–1577 (1911).

† *l. c.*

‡ W. Biltz: Ber., **37**, 1095–1116 (1904).

§ H. Bechhold: Zeit. f. phys. Chemie, **48**, 385–423 (1904).

¶ M. Neisser und U. Friedemann: Münch. med. Wochenschr., **51**, 465–469, 827–831 (1903–4).

proper proportions. Mixtures outside of the precipitating zone do not cause coagulation. The previous generalizations were somewhat enlarged by the discovery that the precipitation zones became larger the less pronounced the colloidal character of the dyestuff; and vice versa, the zones became smaller the slower the diffusion of the dyestuff in question. Table 32 contains a number of examples.

TABLE 32

Janus Green, colloid, basic, $\frac{1}{100}$ per cent is precipitated by the following acid dyestuffs.

Concentration in per cent.	Dyestuff.				
	Highly colloidal.		Moderately colloidal.		Slightly colloidal.
	Congo red.	Nigrosine.	Colloidal.	Slightly.	
$\frac{1}{20}$	−	−	−	−	−
$\frac{1}{60}$	−	−	−	+++	−
$\frac{1}{100}$	−	−	−	+++	+++
$\frac{1}{200}$	−	−	+	+++	+++
$\frac{1}{240}$	−	+++	+++	+++	+++
$\frac{1}{280}$	−	++	+++	+++	+++
$\frac{1}{320}$	−	+	+	+++	+++
$\frac{1}{400}$	+	−	+	+++	+++
$\frac{1}{480}$	+++	−	−	−	+++
$\frac{1}{560}$	−	−	−	−	+++
$\frac{1}{800}$	−	−	−	−	−

+ represents slight; ++ greater; +++ pronounced precipitation.

The numerous tables in the article of Teague and Buxton * go to show that the maximum precipitation occurs when the two dyes are in equivalent amounts. This would indicate that the acid and basic dyes in the solution unite to form a salt which falls out because of its insolubility, just as silver iodide is precipitated from solutions of silver nitrate and potassium iodide mixed together. That the precipitation is not complete when one or other of the substances is in excess has been explained in the discussion on sol formation of silver bromide, page 180. When the cathion and anion have united to form a salt the tendency of the neutral particles is to join together in complexes which finally precipitate out. If, however, one or other of the dyes is present in excess the salt particles adsorb some one ion more than another, and thus attain a positive or negative charge. The charge on the particles increases the stability to such an extent that little or no precipitation may result. If the acid dye is present in excess the particles will

* *l. c.*

become negatively charged because of the adsorption of the dyestuff anion, and vice versa, thus forming a negative or a positive hydrosol respectively. The reactions may be represented by the following equation where DaNa and DcCl represent the two dyes.

$$Dc^+ + Cl^- + Da^- + Na^+ \rightarrow \downarrow DcDa + Na^+ + CL^-.$$

The insoluble combination DcDa would first form ultramicrons that would grow in the solution until a flocculent precipitate would be formed unless some other reaction occurred to arrest the coagulation. If, according to our previous scheme, we represent the ultramicrons in the solution by $\boxed{Dc \cdot Da}$ we can imagine the following to take place:

Adsorption of cathion and therefore a positive hydrosol is formed

$$\boxed{Dc \cdot Da} + Dc^+ \rightleftarrows \boxed{Dc \cdot Da}\, Dc^+.$$

Adsorption of the anion and therefore a negative hydrosol is formed

$$\boxed{Dc \cdot Da} + Da^- \rightleftarrows \boxed{Dc \cdot Da}\, Da^-.$$

The colored ion of highly colloidal dyestuffs, as is well known, is adsorbed by very many substances so that the assumptions underlying the above equations are not at all strained. The wider precipitation zones of dyestuffs having a lesser colloidal character may be explained on the basis of greater solubility of the dye salt formed, and also on the lessened adsorption. We have here relations similar to the precipitation of insoluble inorganic salts, such as barium sulfate, magnesium ammonium phosphate, etc., where sol formation is difficult because large particles form so easily.

That we do not always have to do with ionic reactions, where equivalent quantities unite in the mutual precipitation of dyestuffs, is borne out by the fact that many dyestuff solutions are completely resolved under the ultramicroscope. Indeed the mutual precipitation of dyestuffs is analogous to that of oppositely charged colloids and to the action of electrolytes with regard to precipitation. The author, some years ago, observed that colloidal gold could be precipitated by basic dyestuffs. Sometimes where the concentration relations were suitable the precipitation of gold and Fuchsine or gold and Methyl Violet left a perfectly colorless liquid over the precipitate. It is evidently not a case here of chemical action between Fuchsine and colloidal gold. It was also discovered that the precipitation zone was fairly large, and that, if one constituent was present in excess of the amounts coming in the zone, a protective action occurred. See page 56. The Fuchsine could not be extracted with water, but it dissolved easily in alcohol. The insoluble residue if pressed with an agate pestle had a metallic luster, and therefore consisted of gold.

Protective Effect and Dyestuff Solutions

Dyestuffs as Protective Colloids. — Very interesting observations on a special protective effect which dyestuffs have on solutions of colloidal silver bromide have been made by Lüppo-Cramer.* Eder † had previously demonstrated that the adsorption of dyestuffs by the granules of silver bromide was of importance in the sensitizing of silver bromide. V. Hübl ‡ confirmed and extended Eder's discovery. Lüppo-Cramer § showed that Erythrosine had a very great protective effect on silver bromide hydrosols. Fifty cubic centimeters of the hydrosol containing about 0.2 per cent silver bromide were completely protected by 1 cc. of Erythrosine solution (1 : 400) from the precipitating influence of 5 cc. of a 10 per cent solution of sodium sulfate or potassium nitrate. The mixture remained unchanged for several days, while without the dye precipitation took place in a few moments. Similar protection against ammonia has also been observed. The spontaneous turbidity of silver bromide hydrosols is prevented for weeks by Erythrosine, and even the very unstable silver chloride hydrosols may be kept for a long time if they are but colored with Erythrosine. It also protects the hydrosols against coagulation when the temperature is raised. The pure hydrosols become turbid instantly when the boiling point is reached, but if they are colored with the dye they may be boiled without any change occurring. Strangely enough these crystalloidal Erythrosine solutions do not protect gold hydrosols, according to observations made by the author. It is therefore clear that the specially pronounced protective effect of Erythrosine for silver bromide must be quite different in character from the protective effect of certain colloids such as gelatin toward gold solutions. The protective effect on silver bromide is probably due to the adsorption of the anion of the dyestuff, and this ion prevents somewhat the adsorption of cathion necessary to discharge the ultramicrons. Beside the adsorption of the dyestuff anion, the dyestuff itself is doubtless adsorbed.¶

Dyestuffs Protected with Colloids. — As already stated on page 197 some dyestuffs are very sensitive toward electrolytes. To this group of dyes belong Congo Red and Benzopurpurin, which may be easily coagulated with alkali salts even when the disperse phase is of molecular dimensions. Bayliss || has established the fact that such dye-

* Lüppo-Cramer: Photographische Probleme, 26–33. Halle (1907).

† M. Eders Handb. d. Photogr., **3** (5 Aufl.), 152.

‡ A. v. Hübl: Eders Jahrbuch für, 189 (1894).

§ Miss Stevenson: Koll.-Zeit. (1912).

¶ Zeit. f. Kolloidchemie, **10**, 249 (1912).

|| W. M. Bayliss: Koll. Zeit., **6**, 23–32 (1910).

stuffs may be rendered quite as stable with protective colloids as gold solutions. As protective colloid for Congo Red a dialyzed solution of serum albumin was employed. The dyestuff alone could be immediately precipitated by a solution of N/100 calcium sulfate, but in the presence of the protective colloid the mixture was quite stable. The ultramicroscopic investigation revealed the fact that the particles of the dyestuff partially coagulated had formed a complex (probably due to adsorption) and were thus prevented from falling out.

Dyeing

A series of colloidal chemical investigations is concerned with the behavior of dyestuffs toward fibers. The chief point at issue is whether the coloring of the fibers by the dye is a chemical process, formation of a solid solution, or purely a case of adsorption. Of a large number of articles only a few will be mentioned, namely those of Georgievics,* Appleyard and Walker,† Biltz, ‡ Freundlich and Losev. § In these it was shown that the adsorption isotherms are just as applicable to the taking up of dyes by fibers as by charcoal. In other words the process may be considered as one of adsorption, upon which, in specific instances, solvent and chemical action are superimposed.¶

V. Georgievics has shown that the taking up of Benzidine and some other dyestuffs by fibers could be expressed by the well-known exponential formula ||

$$\frac{x}{m} = \alpha \cdot c^{\frac{1}{n}}.$$

Biltz found similar relations to hold for the taking up of inorganic colloids such as molybdenum blue, colloidal iron oxide, vanadium pentoxide, and some others, by silk and other fibers. The adsorption curves are very similar to those obtained by dyeing with true dyestuffs. He found further that the fibers might be replaced by aluminium hydroxide without causing any material change in the process, but that in some cases the dye was chemically combined, to wit, Alizarine and colloidal iron oxide. Appleyard and Walker have given an interesting example of the differences in quantitative relations between the adsorption of dyes by fibers on the one hand and a chemical union of the

* G. v. Georgievics: Monatshefte f. Chemie, **15**, 705–717 (1894). Ders. und E. Löwy: *Ibid.*, **16**, 345–350 (1895); Sitzungsber. d. Akad. d. Wiss. Wien, **104**, IIb, 309–314 (1895).

† J. Appleyard and J. Walker: Journ. Chem. Soc., **69**, 1334–1349 (1896).

‡ W. Biltz: Ber., **37**, 1766–1775 (1904); **38**, 2963–2977 (1905).

§ H. Freundlich und G. Losev: Zeit. f. phys. Chemie, **59**, 284–312 (1907).

¶ W. Borsche: Med. Naturwiss. Archiv, **2**, 411–422 (1910).

|| H. Freundlich: Zeit. f. phys. Chemie, **57**, 392 (1907).

dye with a crystalloid on the other. If silk is colored with a solution of picric acid in water the equilibrium may be expressed by the exponential function given above. The curves are given in Fig. 31. If the silk is replaced by diphenylamine, which forms a chemical compound with the picric acid, none of the latter is taken up until the concentration has reached 13.8 g. of the acid to one gram water. If more acid is added the diphenylamine takes it up until all the latter is used up, while the concentration of the solution remains constant as long as there exists any diphenylamine. From now on the concentration of the solution increases until the saturation point is reached. Fig. 32 represents the course of the reaction.

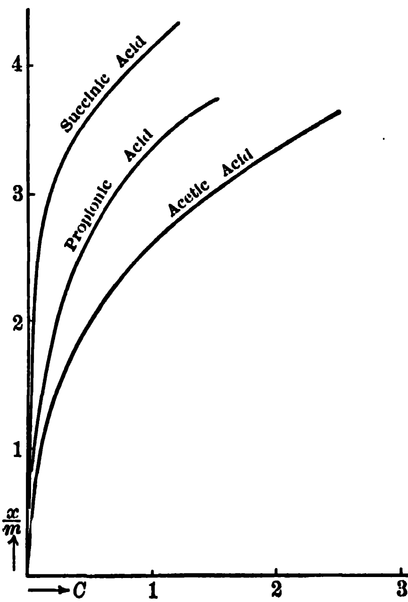


FIG. 31.

In order to explain the curve by the assumption of a chemical combination, one must regard the solid phase as variable. One may also assume that the solid is a solid solution. This is somewhat of a distortion as shown by Freundlich; for, first of all the adsorption equilibrium is reached; and secondly, the adsorption of all sorts of substances follows the same curves where chemical combinations are quite impossible.

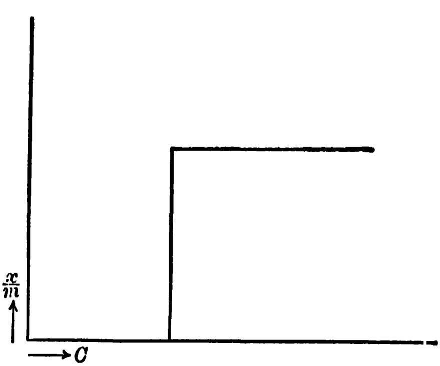
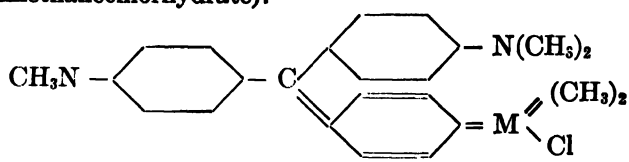


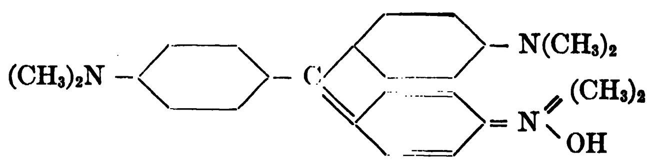
FIG. 32.

Freundlich and Losev have thoroughly studied the taking up of both basic and acid dyestuffs (Crystal Violet, New Fuchsine, etc.) and found that the adsorption of basic dyestuffs differs from that of the acid. In the case of the basic dyestuffs chemical action as well as adsorption takes place. The chemical action occurs on the surface of the charcoal without the latter taking any part. The dyestuff salt adsorbs only the basic dye while the acid remains quantitatively in solution. The base suffers a change, probably into an isomeric modi-

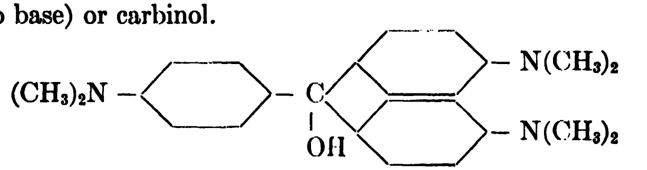
fication, becomes insoluble in water, but can be dissolved in benzol or alcohol. According to Hantzsch * such transitions also occur when solutions of triphenylmethane dyestuffs are treated with alkalis. An especially good case is that of Crystal Violet (hexamethyltriamidotriphenylmethanechlorhydrate).



When to one mol. of the dyestuff one mol. of potassium hydroxide is added the Cl is replaced by OH and a true soluble base is obtained.



This base like the dyestuff is colored, shows a basic reaction, and is therefore dissociated in solution. Gradually the solution becomes colorless, does not react basic, and contains the ordinary dyestuff base (Pseudo base) or carbinol.



During adsorption something else occurs. The adsorbed dyestuff has the same color as that of the solution, but the surface of the charcoal has a brownish luster. The adsorbed material gives a brown solution in benzol, while the solution colors paper or alcohol violet. A further or different change must have taken place.

It is possible that a similar colored base is formed when wool is dyed by Fuchsine. The well-known experiment where the colorless Fuchsine base (pseudo-base) colors wool deep red may be explained by some such change. Usually the red color is attributed to the formation of a salt by the union of the base with the wool. Such a salt formation is not improbable because animal fibers contain amido and carboxyl groups that might unite with the dyestuff base. Suida and Gelmo † favor this view, according to which the reaction is an esteri-

* A. Hantzsch und G. Osswald: Ber., **33**, 278–317, 752–760 (1900).

† W. Suida und P. Gelmo: Monatshefte f. Chemie, **26**, 855–878 (1905); **27**, 225–235, 1193–1198 (1906).

fication. In the light of the existence of the adsorption isotherms it is still questionable whether the fast dyeing of wool and silk is due to chemical reactions or to mere adsorption. In favor of the latter view is the fact that vegetable fibers take up dyestuff salts, such as Benzidine, and others. There seems to be less likelihood of chemical reactions taking place here. The researches of Weber * point toward adsorption. According to these investigations the dyeing of vegetable fibers depends upon the structure of the latter. Cotton fibers are flattened tubes with thick walls. These walls are not colored by the dye, but the latter penetrates them and is precipitated in the tiny tubes. Fibers that have no central canal (dead fibers) are not colored by the dye. Weber has given further evidence of this peculiar behavior on the part of fibers. Dinitrocellulose can be colored just as the ordinary cellulose. If the nitrocellulose is dissolved and the solvent evaporated away the residue is not colored by the dye.

Georgievics † has recently stated that for the taking up of acid and basic dyestuffs in very dilute solution $\frac{C_{\text{fiber}}}{C_{\text{acid}}}$ is a constant. That is to say Henry's law obtains in very dilute solution. That the same law holds for the condensation of gas on the surface of charcoal at low pressure has long been known.‡ It is probable that we have to do here with a general law.

Capillary Analysis

As shown by Schoenbein,§ dissolved substances rise to different heights in strips of unglazed paper. Usually the water precedes the dissolved substance but the height of the latter is not always the same. Strips of filter paper were hung in three solutions containing turmeric dye. The first solution contained sodium hydroxide, the second barium hydroxide, and the third calcium hydroxide. The brown color rose seven-tenths of the height of the water in the first vessel, three-tenths in the second, and one-tenth in the third. Similar results were obtained with solutions of dyestuffs; the dye followed the water up the paper but to different heights.

As pointed out by W. Ostwald ¶ the cause is to be sought in the

* C. O. Weber: Lehnes Farberzeitung, **5**, 161, 184, 201, 214 (1893–4).

† G. v. Georgievics: Sitzungsber. d. Akad. d. Wiss. Wien, **120,** IIb, 857–869 (1911).

‡ M. W. Travers: Zeit. f. phys. Chemie, **61,** 241–248 (1908). W. McBain: *Ibid.*, **68,** 471–497 (1910). A. Titoff: *Ibid.*, **74,** 641–678 (1910). Ida Fr. Homfray: *Ibid.*, **74,** 129–201 (1910).

§ C. F. Schoenbein: Verh. d. Naturf.-Ges. Basel, III Teil, 249–255 (1863).

¶ W. Ostwald: Lehr. d. allg. Chemie (2 Aufl.), **1,** 1095. Leipzig (1905).

adsorption of the various materials. Goppelsroeder * has carefully studied these relations and has devised an analytical separation that has a wide application in work on dyestuffs, alkaloids, and oils. An investigation by Fichter and Sahlbom † has shown that negatively charged colloids rise in strips of paper and the positively charged are precipitated at the dipping surface. The authors attribute the precipitation to the presence of currents in the capillaries of the paper. In glass capillaries also the water rises higher than basic dyestuffs and positive colloids.

TABLE 33

From Pelet-Jolivet

Effect of	Electrical charge by contact. (Perrin.)	Coagulation.	Coloring of fibers.	Rise in capillaries.
Acids.....	Increase charge on positive surfaces	Increase stability of positive colloids	Decrease coloring by basic dyes	Increase rise of basic dyes
	Decrease charge on negative surfaces	Coagulate negative colloids	Increase coloring by acid dyes	Decrease rise of acid dyes
	All acids having the same H ion concentration work alike			
Bases......	Bases have the reverse effect (exception in case of acid dyes)			
Salts	Ions with the opposite sign reduce charge on a surface	Ions of opposite charge cause coagulation	Ions with opposite charge increase coloring	Ions with opsite charge decrease rise
	May reverse charge	Colloid may become oppositely charged	....	....
	Higher the valence the greater the effect	The ions with higher valence have the greatest effect		
	In general ions with higher valence do not increase the charge on a surface having the same sign	Ions of same sign increase stability	Ions with same sign decrease coloring	Ions with same sign increase rise of basic dyes but not of acid dyes

* F. Goppelsroeder: Kapillaranalyse. Basel (1906).

† F. Fichter und N. Sahlbom: Koll.-Zeit., 8, 1–2 (1911).

Elaborate investigations by Pelet-Jolivet * and his collaborators resulted in the discovery of interesting relations between the rise in capillaries, on the one hand, and dyeing, coagulation, and electrical charge by contact, on the other. Some of these relations are presented in Table 33.

The results in the table may be summarized as follows: All the influences that tend to discharge the particles increase the power of the dye to color the fiber and decrease the rise in capillaries. On the contrary, influences tending to increase the stability of the colloidal dyestuff, increase of dispersion, etc., work in the opposite direction.

* L. Pelet-Jolivet: Koll. Zeit., 5, 238–243 (1909).

CHAPTER XII

PROTEIN BODIES

PROTEIN bodies are the most important substances in plant and animal tissues. They are thoroughly discussed in works on physiological chemistry and will not be taken up here except in their relation to colloidal chemistry. For this purpose the properties of typical members of the more important groups will be dealt with.

All proteins are produced in plants or animals. They contain C, H, O, N, and S in fairly constant proportions and are of a most complicated molecular structure, in which the amino-acids play an important part. Some of them are reversible and some irreversible colloids.

I. *Simple Proteids, or Albuminous Bodies.* — To this group belong the simple, genuine proteids in the narrower sense of the word. These can be coagulated easily. Albumins and globulins come under this heading.

II. *Compound Proteids.* — These are combinations of proteids with other bodies and have peculiar properties due to these latter called "prosthetischen Gruppen" by Kossel. To this prosthetic group belong nucleinic acid in nucleoproteids, hemitin in hemoglobin, carbohydrates or their derivatives. These substances may be separated by the action of acids.

III. *Albumoids or Albuminoids.* — These substances are not a part of the cell but form a ground substance in which the cells lie. They have special properties that justify a distinction being made between them and other proteids, although the composition of the bodies into which they can be separated places them with the many proteids.

Specially characteristic is their insolubility in water, salt solution, and in liquids from animal bodies. Most of them are scarcely soluble in dilute alkalis.

Simple Proteids or Albuminous Bodies.

These substances form the chief constituents of the blood, the muscles and glands. They are contained in most of the secretions and excretions of the body but are not present in tears, perspiration, nor in normal urine. They all contain C, H, N, O, S, and some have a small amount of phosphorus and iron. The composition varies generally between the following limits:

	Per cent
C	50.6 to 54.4
H	6.5 to 7.3
N	15 to 17.6
S	0.32 to 2.2
P	0 to 0.85
O	21.5 to 23.5

Simple proteids are odorless, tasteless, generally amorphous but sometimes crystalline. Their solutions are optically active and rotate the plane of polarization to the left. They unite with either acids or bases and therefore resemble amphoteric electrolytes. They are weak both as acids or bases and have a large valence number. Otherwise they behave in a manner similar to certain colloids such as stannic acid or the purple of Cassius.

1. Classification

A classification according to constitution is not yet possible; it is not well enough understood. In physiological chemistry a classification has gradually come into use that gives a survey of the field. The classification of Cohnheim * has been chosen, which is also similar to that of Hammarsten,† Hoppe-Seyler,‡ and Drechsel.§

We are not justified in considering the combination of proteids with acids or alkalis as salts. Rather must we consider that similar relations exist as in the case of the purple of Cassius. On the other hand it cannot be denied that the purely chemical point of view has much in its favor, especially with regard to the decomposition products which consist principally of aminoacids, amphoteric electrolytes. In this consideration the colloidal nature of the proteids must not be lost sight of, for ultramicrons appear in quantity in the case of the most important members.

The precipitation of proteids by concentrated solutions of alkalis is generally reversible. This is the principle employed in many methods for separating them from one another. Precipitation with salts of the heavy metals is generally irreversible. Often here irregular behavior is met with that is due to peptisation of the precipitate by the salts. A survey of the simple proteids is given in Table 34.

* O. Cohnheim: Chemie der Eiweisskörper. Braunschweig (1904).

† O. Hammersten: Lehbuch der physiologischen Chemie. Wiesbaden (1907).

‡ F. Hoppe-Seyler: Handbuch der physiologisch-und pathologisch-chemischen Analyse (7. Aufl.). Berlin (1903).

§ E. Drechsel: Artikel "Eiweisskörper" in Ladenburgs Handwörterbuch der Chemie, 3, 534 (1885).

TABLE 34

TRUE PROTEIN BODIES

1. Albumins (serum, egg, lacto-albumins).
2. Globulins (serum, egg, cell globulins).
   a. Plant protein (plant globulins).
   b. Fibrinogen, and fibrin, from the blood plasma of the mammals.

By fibrin ferment these are changed into fibrin, and occasion the coagulation of the blood.

   c. Myosin and myogen, muscle protein. Probably the cause of rigor mortis is the coagulation of myosin under the influence of a ferment.

3. Phosphorus containing proteins (nucleo-albumin or phosphorus globulin), acid protein, as casein, vitelline of the yolk of eggs, nucleo-albumin of the cell protoplasma, etc.

4. a. Histones, basic protein, precipitated by alkalis; found in blood corpuscles of geese.

   b. Protamines, proteins free from sulfur, but rich in nitrogen, in the sperma of salmon.

Albumins. — Albumins are the richest in sulfur of all proteids, containing from 1.6 to 2.2 per cent S. They are soluble in water and are not precipitated at ordinary temperature by dilute solutions of alkalis, acids nor concentrated solutions of NaCl or $MgSO_4$. Saturated solutions of $(NH_4)_2SO_4$ precipitate them completely. They are not coagulated at boiling temperatures unless considerable neutral salts are present.

Globulins. — Globulins are peculiar protein bodies that are soluble in dilute solutions of neutral salts, but not in pure water. Dialysis, filtration through Bechhold's filter, or great dilution precipitates them. They are again dissolved by traces of alkali, while neutralization of the solutions separates them out again. Concentrated solutions of NaCl or $MgSO_4$ precipitate them partially or completely. Half-saturated solutions of $(NH_4)_2SO_4$ also precipitate them.

The separation of proteids is made easier by the fact that specific liquids of the body contain only certain of the proteids. Thus egg albumin contains globulin, albumin and ovomucoid; blood plasma contains fibrinogen, globulin and albumin. As an example of how the separations are carried out the isolation of certain members from the blood plasma may be cited.

Horse blood is prevented from coagulating by the addition of one-tenth volume of 1 per cent $(NH_4)_2C_2O_4$ and the blood corpuscles are allowed to fall as sediment to the bottom. Next 3 parts of a saturated solution of $(NH_4)_2SO_4$ to 7 parts of plasma are added, whereby fibrinogen is precipitated. The solution contains globulin and albumin. Four parts of saturated $(NH_4)_2SO_4$ solution are now added to 10 parts of the solution and globulin separates out. The albumin can be precipitated by saturating the filtrate with solid $(NH_4)_2SO_4$. The different fractions may be purified by washing with the corresponding salt solutions and then dialyzing. If acid is carefully added with the

$(NH_4)_2SO_4$ until the solution begins to be turbid the albumin may be obtained in a crystalline form.

The separation of proteids in the white of eggs is achieved by a similar process. $(NH_4)_2SO_4$ is added until the solution is one-half saturated in order to precipitate the globulin. The filtrate contains albumin and ovomucoid. A part of the former may be obtained in crystalline form by adding acid until the liquid becomes turbid. After standing 24 hours microscopic crystals of egg albumin are obtained that may be further purified by recrystallization. The state of purification can be best determined by means of the gold number, page 106. Further additions of $(NH_4)_2SO_4$ to the filtrate precipitate more albumin in amorphous form. These fractions do not appear to be amorphous modification of the crystalline albumin, but differ from the latter in both chemical and physical properties.

It should be noted that globulins are by no means simple uniform substances. By suitable reactions they also may be fractionated into different bodies.

Compound Proteids and Albuminoids

Survey of Compound Proteids and Albuminoids

a. Compounds of proteids with bodies not proteids.

1. Nucleoproteids; proteids with nucleinic acid.
2. Hemoglobins and related substances; globins with Hematin.
3. Glycoproteids (Mucines, Mucoids; compounds of proteids with carbohydrates).

Nucleoproteids are constituents of the cell nuclei and may be separated with proteids and nuclein, or proteids and nucleinic acid. The latter may be separated into pyramidins and purine derivatives among other substances. Hemoglobins will be taken up later. To the glycoproteids belong, among other bodies, ovomucoid that is not easily coagulated.

b. Albuminoids.

1. Keratin (horny substances of the human and other animal bodies).
2. Kollagen.
3. Elastins (constituents of elastic tissues).
4. Fibroin (contained in the fibers of silkworm).
5. Spongin (found in the structure of the common sponge), Amyloid, Albuminoid.

As already stated the albuminoids form the structure tissues of animals and differ from ordinary proteids in their great stability toward

solvents and chemical influences. Keratin is the chief constituent of the outlayer of the epidermis, hair, feathers, horns, hoofs, and nails.

Kollagen. — The fundamental substance of the bones and cartilages. By long boiling in water, faster in dilute HCl, kollagen goes into glutine, glue, or gelatine.

Decomposition Products of Protein Bodies

Survey

1. Acid Albumins and Alkali Albuminates.

By treating proteids with alkalis or acids, decomposition products are obtained that are closely related to the proteins. They are called alkali albuminates and acid albumins, or syntonins. Paal * obtained his protalbinic and lysalbinic acids by treatment of proteids with alkalis. The former are closely allied to alkali albuminates and the latter to the albumoses. The alkali albuminates are excellent protective colloids; so are protalbinic and lysalbinic acids. The gold number of the sodium salt of protalbinic acid is 0.03 to 0.08 while that of lysalbinic acid is 0.02 to 0.06. Concerning their use in the preparation of colloidal metals see Chapter V.

a. Pepsin Digestion. — Albumoses and peptones are generated by the pepsine digestion of proteids. Stomach juices contain enzymes together with mucous substances, salts and HCl (0.4 per cent). Pepsin is one of the most important of these enzymes and is active for digestive purposes only in the presence of HCl. Not only natural proteids undergo digestion but also denatured proteids such as coagulated proteid. Distention occurs first and then dissolution. The maximum temperature at which pepsin digestion takes place is slightly higher than the temperature of the body, *viz.*, at 40° C. Syntonins and primary albumoses are first formed; then secondary albumoses and finally peptones, the end product of pepsin digestion.

Albumoses diffuse slowly in aqueous solutions, not at all or only partially through membranes, and Bechhold's filter retains them. Saturated $(NH_4)_2SO_4$ precipitates them. Peptones, on the other hand, resemble the crystalloids much more. They diffuse fairly easily, pass through membranes slowly, and are not precipitated by $(NH_4)_2SO_4$. In contradistinction to peptones, albumoses and peptones do not coagulate on boiling.

Albumoses and peptones may be separated by the following scheme:

* C. Paal: Ber., **35**, 2195–2206 (1902).

50 cc. albumose solution
+ 50 cc. saturated $(NH_4)_2SO_4$.

Ppt. I (Primary albumoses)
Dissolved in H_2O and dialyzed

Ppt. II
Heteroalbumoses

Filtrate
Protalbumoses

Filtrate I
Add solid $(HN_4)_2SO_4$

Ppt. secondary
Albumoses

Filtrate
Peptones

The products of pepsin digestion were previously called peptones regardless of whether they contained albumoses or not. The larger part of Witte-peptone procurable on the market consists of albumoses. According to Bechhold it is possible to separate albumoses from one another by filtration. The glacial acetic acid collodion filter retains the primary albumoses, while the deuteroalbumoses pass through. These may be filtered out by a 8 to 10 per cent filter. Albumoses are frequently called proteoses at the present time.

Heteroalbumoses, obtained by dialysis in the above scheme and therefore behaving similarly to globulin, have a high gold number (according to Zunz, 0.01 to 0.075). Protalbumoses are much less efficacious as protective colloids; gold number 1.6 to 3.4. Secondary albumoses and the majority of the peptones have the property of turning red colloidal gold solutions blue without the help of other electrolytes, see Chapter V. Neither albumoses nor peptones are simple substances. By alcohol they may be further fractionated, but even these products are also mixtures.

b. Pancreas Digestion. — Trypsin, a ferment found in the intestines, causes a considerable splitting of the proteid products to aminoacids (leucin tyrosin, asparaginic acid, tryptophanes, etc.). Pancreas digestion takes place in alkali reaction and changes deuteroalbumoses to anti- and hemi-peptone; the latter is split into aminoacids.

The chemistry of proteins has received a very decided advance by the excellent work of Emil Fischer and his collaborators through the synthesis of polypeptides from amino-acids. For a detailed account of the polypeptides reference should be made to works on physiological chemistry.

2. General Behavior of Protein Bodies

Osmotic Pressure

Careful osmotic pressure investigations on protein bodies have been made by Hüfner and Gausser (see hemoglobin, page 231), Moore and his collaborators,* and by Lillie.† Moore and Roaf have shown that

* B. Moore and W. H. Parker: Amer. Journ. of Physiol., **7**, 261 (1902). The same with H. E. Roaf: Biochemical Journ., **2**, 34 (1906).

† R. S. Lillie: Amer. Journ. of Physiol., **20**, 127–169 (1907).

the osmotic pressure of gelatin solutions increases more rapidly with the temperature than would be predicted from the laws of solutions. This agrees with the tendency of gelatins to form larger complexes and finally to harden as the temperature is lowered. These authors have also observed interesting hysteresis phenomena. (See gelatins, page 223.) Lillie investigated the osmotic pressure of egg albumin, and also the effect of the addition of crystalloids to gelatin solutions. The proteins were put in the collodion sack of the osmometer (page 35) and the pressure against pure water measured. The maximum height of the column was reached in about 20 hours, and remained constant for several hours. The influence of the crystalloids was determined by adding amounts to both the inner and outer liquids until the concentration in each was equal. In doing this great care must be taken with regard to stirring, etc., in order to avoid irregular results.

TABLE 35

Egg albumin at room temperature.	Pressure in mm. Hg.
1.25 per cent egg albumin..........	22.4
+ $\frac{1}{6}$ mol. cane sugar................	21.5
+ $\frac{1}{6}$ mol. dextrose..................	21.8

Nonelectrolytes show little influence on the osmotic pressure of protein or gelatin solutions. Cane sugar, dextrose, glycerine, urea, each to the amount of 1.25 per cent, were added to a gelatin solution. The column stood at 6.2 mm. without the addition. Urea raised it to 7.3, while glycerine and dextrose gave 5.8 and 5.9 respectively. The effect of the addition on egg albumin can be seen in Table 35.

TABLE 36

Gelatin 1.5 per cent.			
Without HCl.	8.2 mm. Hg.	Without KOH.	6.2 mm. Hg.
$\frac{N}{3100}$	6.8	$\frac{N}{3100}$	6.1
$\frac{N}{2050}$	12.3	$\frac{N}{1240}$	27.4
$\frac{N}{1550}$	17.9	$\frac{N}{620}$	33.1
$\frac{N}{770}$	32.4	$\frac{N}{310}$	33.2
$\frac{N}{422}$	39.3	....	....

On the contrary the influence of electrolytes is considerable. The presence of acids and alkalis causes the ultramicrons of gelatin to subdivide, and the column to rise in consequence as seen in Table 36.

In the case of egg albumin the acid (HCl) caused a fall at first and then a rise.

TABLE 37

HCl.	Pressure in mm. Hg.	HCl.	Pressure in mm. Hg.
D	25.6	$\frac{N}{620}$	20.4
$\frac{N}{3100}$	20.7	$\frac{N}{310}$	22.2
$\frac{N}{1240}$	11.5		

The effect of HCl on gelatin can be explained only on the ground of a subdivision of the ultramicrons and simultaneous or subsequent ionization. The subdivision is rendered more probable by the fact that submicrons are visible in gelatins at ordinary temperatures. This behavior of gelatin with HCl agrees with experiments of Wo. Ostwald * who found that small amounts of HCl decrease the distention while large amounts increase it very greatly. Alkali also increases the distention.

One might assume that acids and alkalis cause the decomposition of the gelatin molecule into albumoses and peptones and therefore the pressure must increase. Against this assumption is the experimental fact of the small concentration of the HCl; and secondly that the original pressure is almost entirely restored after the removal of the HCl by dialysis. Neutral salts, contrary to the effect of acids, lower the osmotic pressure of both gelatin and albumin solutions. This is in accordance with the fact that neutral salts have a coagulating effect on protein solutions long before the precipitating concentration is reached. The number of particles is lessened and therefore the osmotic pressure decreased. The influence is apparent from the following table.

TABLE 38

NaCl.	*RD.*	NaCl.	*RD.*
$\frac{n}{12}$	0.18	$\frac{n}{48}$	0.26
$\frac{n}{24}$	0.23	$\frac{n}{96}$	0.37

$$RD = \frac{\text{Osmotic pressure of the salt solution}}{\text{Osmotic pressure of the original solution}}.$$

Wo. Ostwald: Pflügers Archiv. f. d. ges. Physiol., **108**, 563–589 (1905).

Several hundred experiments were carried out to determine the relation between the fall in pressure and the nature of the electrolyte. It turned out that both the nature of the anion and that of the cathion are factors. Hofmeister * and Pauli † have arranged several anions in the descending order of their reducing effect on the osmotic pressure of protein solutions. $SO_4 > Cl > NO_3 > Br > I > CNS$. Both series of experiments point to the conclusion that the reduced pressure is due to partial coagulation of the particles.

Pure protein solutions lose very little of their osmotic pressure through violent shaking. If electrolytes are present the pressure is reduced from 10 to 20 per cent.

Lillie ‡ has found that the increase of osmotic pressure with the concentration is not quite proportional, the pressure increasing faster than the concentration. This result is in agreement with the fact that many proteids, such as globulin, are precipitated by diluting, whereby the number of particles is lessened and therefore the pressure lowered beyond the normal amount. Duclaux obtained similar results with colloidal iron oxide solutions, but the explanation is doubtless different from that in the case of proteids. See page 167.

Precipitation of Proteids with Electrolytes

The precipitation of proteids by electrolytes has been especially well investigated by Hofmeister § and his students. It is shown that the precipitation of egg or serum albumin by alkali or magnesium salt mixtures is reversible; that is the precipitates will dissolve in water on the removal of the salt. Large amounts of the salt are necessary for precipitation. Salts of the alkaline earth metals in large amounts also cause precipitation, but the precipitate rapidly becomes insoluble. Lower concentrations cause a reversible precipitation and the precipitate is redissolved by concentrations somewhat greater.

In connection with the precipitation by salts of the alkali metals it was found that the anions had a distinct effect. With the same cathion the tartrate had a greater effect than the sulfate, and so on. The series is given below:

Citrate > Tartrate > Sulfate > Acetate > Chloride > Nitrate > Iodide > Sulfocyanate.

* F. Hofmeister: Archiv. f. experim. Pathol. u. Pharmakol., **24,** 1–30 (1889).

† W. Pauli: Hofmeisters Beiträge z. chem. Physiol. u. Pathol. **3,** 225–246 (1902).

‡ Lillie: *l. c.*

§ S. Lewith: Archiv. f. experim. Pathol. u. Pharmakol., **24,** 1–16 (1888). F. Hofmeister: *Ibid.,* **24,** 247–260; **25,** 1–30 (1889).

It will be seen that this series agrees with that of Lillie given on page 216. The iodide and sulfocyanate do not cause coagulation at all. Posternak * and also Pauli † have found that the series is reversed if the experiments are carried out in slightly acid solution. There iodides and sulfocyanates have the greatest precipitating effect while citrates have the least. In strongly acid solutions the precipitation is not reversible; that is the precipitate will not dissolve in pure water. In dilute alkali solutions the series has the same order that it has in neutral solutions. In both cases the particles are charged negatively, but are charged positively in acid solution.

Pauli ‡ found that there was a relation between the precipitating effect on protein bodies and the physiological effect. Citrates, tartrates, and sulfates excite the intestines and raise the blood pressure, while nitrates, bromides, and sulfocyanates lower the blood pressure. Iodides and sulfocyanates cause side reactions that result in colds in the head and in acne

Neutral Proteids

Pauli§ has succeeded in taking a further step in this field by preparing a proteid hydrosol almost free from electrolytes. This hydrosol, obtained by dialyzing for 8 days has somewhat different properties from the ordinary proteid solution. It coagulates completely on boiling without the presence of electrolytes, and suffers irreversible precipitation by alcohol. It does not migrate in the electric current, or at least very little. Pauli has called this preparation neutral or amorphous proteid. He determined by migration experiments that acids charge it positively and alkalis negatively. Hardy ¶ had previously recorded the same effects of acids and alkalis on proteid solutions. The influence of acids and alkalis on the direction of the migration is therefore independent of the size of the particles.

A series of phenomena are in agreement with the electrical charge, or the ionization of these amphoteric proteids. The viscosity increases with small additions of HCl, $\frac{n}{100}$ HCl causing a change in the inner friction of 1068 and 1209. Pauli attributes this to hydration of the ultramicrons because of their ionization. Other properties also change, for while amorphous proteid can be precipitated with alcohol a slight amount of acid or alkali prevents this. Larger amounts of acids

* S. Posternak: Annales de l'institut Pasteur, 15, 85 ff. (1901).

† W. Pauli: Hofmeisters Beiträge z. chem. Physiol. u. Pathol., **5**, 27–55 (1903).

‡ W. Pauli: Wiener klin. Wochenschr, Nt. 20 (1904).

§ W. Pauli: Beiträge z. chem. Physiol. u. Pathol., **7**, 531–547 (1906).

¶ W. B. Hardy: Zeit. f. phys. Chemie, **33**, 385–400 (1900).

restore the normal precipitation, probably because of the driving back of the dissociation. As explained on page 219, $NaCl$ and $NaNO_3$ and other neutral salts have a similar effect. Conductivity measurements have shown that the charge on the particles was reduced by these salts.

Electric Charge on the Proteid Particles

The particles of neutral proteid of Pauli, boiled hydrosols, or suspensions of proteids (but not coagulated suspensions with submicroscopic particles) are charged positively by acids and negatively by alkalis. In general the charge may be caused by the adsorption of the hydrogen or hydroxyl ion according to the following scheme:

$$\boxed{U} + H^+ \rightleftharpoons \boxed{U}\, H^+.$$
$$\boxed{U} + OH^- \rightleftharpoons \boxed{U}\, OH^-.$$

In most cases it is more probable that the acid or alkali forms a chemical combination with some of the surface molecules and these give forth ions. The remaining ultramicron would therefore be charged.

It is known that a neutral salt may be adsorbed without affecting the direction of migration.

$$|U| + Na^+ + Cl^- \rightleftharpoons |U \begin{smallmatrix} Na^+ \\ Cl^- \end{smallmatrix}.$$

This adsorption, or possibly chemical combination, may influence the solubility and other chemical properties, while it does not affect the charge.

Proteids, containing as they do both amido- and carboxyl groups, resemble amino-acids (out of which they are partly made) to a large degree in their chemical behavior. It is well therefore to consider some of their chemical reactions as Hardy * and Pauli † have done. According to Pauli the presence of the amido- and carboxyl groups may be represented thus:

$$R\begin{matrix} \diagup NH_2 \\ \diagdown COOH \end{matrix}$$

Every molecule contains several amido and hydroxyl groups and therefore every ultramicroscopic complex must contain many more. For the sake of simplicity let us consider only one of these groups.

If an amine, $R \cdot NH_2$, and HCl come into contact an ammonium salt will be formed.

$$R \cdot NH_2 + HCl \rightleftharpoons RNH_3Cl.$$

This salt is dissociated in solution:

$$RNH_3Cl \rightleftharpoons RNH_3^+ + Cl^-.$$

* W. B. Hardy: Journ. of Physiol., **33**, 251–337 (1905–1906).

† W. Pauli und H. Handovsky: Biochem. Zeit. **18**, 340–371 (1909).

Similarly an amido group and HCl would form a salt:

$$R\begin{matrix}\diagup NH_2\\ \diagdown COOH\end{matrix} + HCl \rightleftharpoons R\begin{matrix}\diagup NH_3Cl\\ \diagdown COOH\end{matrix} \rightleftharpoons R\begin{matrix}\diagup NH_3^+\\ \diagdown COOH\end{matrix} + Cl^-.$$

Or simply:

$$R\begin{matrix}\diagup NH_2\\ \diagdown COOH\end{matrix} + H^+ \rightleftharpoons R\begin{matrix}\diagup NH_3^+\\ \diagdown COOH\end{matrix}$$

Vice versa a neutral proteid is charged negatively by NaOH.

$$R\begin{matrix}\diagup NH_2\\ \diagdown COOH\end{matrix} + OH^- \rightleftharpoons R\begin{matrix}\diagup NH_2\\ \diagdown COO^-\end{matrix} + H_2O.$$

It makes little difference in the point of view whether we consider the radicle $R \begin{matrix}\diagup\\ \diagdown\end{matrix} \frac{NH_2}{COOH}$ on a single molecule or on an ultramicron. In the latter case our equation would be written

$$\boxed{U}\, R\begin{matrix}\diagup NH_2\\ \diagdown COOH\end{matrix} + OH^- \rightleftharpoons \boxed{U}\, R\begin{matrix}\diagup NH_2\\ \diagdown COO^-\end{matrix} + H_2O.$$

That the acids are really bound to the proteids has been demonstrated by Sjöquist,* Cohnheim,† and others. Bugarszky and Liebermann ‡ showed that at higher concentrations both the H^+ ion and Cl^- ion were bound, also similarly NaOH. Barratt § has shown that both H^+ and OH^- are bound by living protoplasm.

As already stated the electrically charged particles are to be regarded as the cause of the increased viscosity in protein solutions (Laqueur and Sackur,¶ Hardy, Pauli, and others) and Pauli assumes the greater hydration of the proteid molecules, or ion molecules. The union of the water with the proteid is not necessarily a chemical one in the strict sense of the word. The hydrate formation corresponds to the stability of the hydrosol toward alcohol. If the charge is neutralized the proteid gives up the water and becomes precipitable by alcohol.

As stated on page 218 large concentrations of HCl precipitate the proteid ionized by small amounts of this acid. This may be explained on the ground that ionization of the acid drives back the ionization of the proteid complex, and therefore it is less stable. NaCl would have

* J. Sjöquist: Skand. Archiv. f. Physiol., **5,** 277–376 (1895).

† O Cohnheim: Zeit. f. Biol., **33,** 489–520 (1896). Ders. und H. Krieger: *Ibid.*, **40,** 95–116 (1900).

‡ S. Bugarszky und L. Liebermann: Archiv. f. d. ges. Physiol., **72,** 51–74 (1898).

§ J. O. Wakelin Barratt: Zeit. f. allg. Physiol., **5,** 10–33 (1905).

¶ E. Laqueur und O. Sackur: Hofmeisters Beiträge z. chem. Physiol. u. Pathol., **3,** 193–224 (1903).

a similar effect, or in fact any neutral salt. In the latter case, according to Hardy and also Pauli, hydrogen ion will be set free. In other words the metal ion will be substituted for the hydrogen ion in the complex as shown in the following schemes according to Hardy:

$$R\left\langle\begin{array}{l} NH_2\left\langle\begin{array}{l}H\\ Cl\end{array}\right.\\ COOH\end{array}\right. + NaNO_3 \rightarrow R\left\langle\begin{array}{l} NH_2\left\langle\begin{array}{l}Na\\ Cl\end{array}\right.\\ COOH\end{array}\right. + HNO_3.$$

Pauli holds the following reaction to be the more probable:

$$R\left\langle\begin{array}{l} NH_2\left\langle\begin{array}{l}H\\ Cl\end{array}\right.\\ COOH\end{array}\right. + NaNO_3 \rightarrow R\left\langle\begin{array}{l} NH_2\left\langle\begin{array}{l}H\\ Cl\end{array}\right.\\ COONa\end{array}\right. + HNO_3$$

Precipitation with the Salts of Heavy Metals

Precipitation with this class of salts differs from that with the alkali salts in that small amounts of the former are sufficient, and that the precipitate is insoluble in water. The process recalls the irreversible precipitation of colloids where likewise a small amount of the salt caused the colloid to become insoluble in water. Without going into the discussion of a possible chemical combination the process may be represented thus:

$$\boxed{E}^{--} + Zn^{++} \rightleftarrows \boxed{E}\ Zn.$$

In case that the charge on the proteid complex was due to the dissociation of hydrogen ion, the neutralization by the metal ion would not set any more acid free.

The precipitate is sometimes soluble in an excess of the precipitating agent. This solubility may be caused by peptisation, or may be considered in the same light as the formation of complex ions. Szillard * has assumed peptisation to be the cause, for he succeeded in peptising coagulated proteids with the salts of heavy metals, such as uranylnitrate, thorium nitrate, zinc and copper sulfates, although the two latter required a large quantity. To explain this from the colloidal chemical standpoint it is but necessary to assume that the coagulated particles take more zinc ion and become charged again, but this time positively. The equation would be as follows:

$$\boxed{E}\,\big|\,Zn + Zn^{++} \rightleftarrows \boxed{E}^{Zn^{++}}_{Zn}$$

The peptised colloid is positively charged. As in the case of zinc sulfate very often a still larger excess will cause a second precipitation.

* B. Szillard: Journ. de chim. phys., 5, 495–496 (1907).

Frequently the solubility of the salt in question is not great enough to cause the second precipitation; *i.e.*, copper sulfate. The precipitation of proteids by zinc sulfate recalls the irregular series of Bechhold,* Neisser and Friedemann.† Silver nitrate and many other salts of the heavy metals cause irreversible precipitation of proteids, and the precipitate is not soluble in an excess of the reagent.

Coagulation and Denaturization of Proteids

When proteids are raised to the boiling point they suffer specific changes of two kinds: they either separate out as a curd in the normal way, or they remain dissolved as a colloid with other properties. The visible change during the formation of the curd or precipitate is favored in a large degree by the presence of salts and traces of acid (Koch test for proteids.) Moderately dialyzed proteids do not coagulate on boiling, and no visible action takes place with traces of alkalis and acids. Boiled solutions of proteids relatively free from electrolytes can be brought to visible coagulation immediately by the addition of neutral salts. These differ from the original solutions in that they are filled with innumerable submicroscopical particles. In general behavior they resemble the irreversible colloids. If such a solution is made alkaline the particles are charged negatively and the valence of the cathion is a factor in the precipitation.‡ On the contrary the anion is the important factor if the colloid has been charged positively by the addition of acid.

Pauli and Handovsky§ have observed an interesting case of denaturization. Small quantities of salts of the alkali and alkaline earth metals raise the coagulation temperature of well-dialyzed proteid solutions; in other words tend to prevent coagulation by heat. If higher concentrations of salts are employed the alkali salts may be divided into three groups that differ in their effect on the coagulation temperature. One group is comprised of iodides and sulfocyanates, which in higher concentration completely prevent coagulation. This is interesting and it was a question whether the iodide prevents the denaturization of the proteid by heat, or prevents the precipitation of the denatured proteid. Experiment showed that the latter was the case, and that the heat actually causes the denaturization. By dialysis the excess of salt was removed and coagulation occurred immediately.

* H. Bechhold: Zeit. f. phys. Chemie, **48**, 385–423 (1904).

† M. Neisser und U. Friedmann: Münch. med. Wochenschr., **51**, 465–469, 827–831 (1904).

‡ Hardy: *l. c.*

§ W. Pauli und H. Handovsky: Hofmeisters Beiträge z. chem. Physiol. u. Pathol., **5**, 27–55 (1903).

Proteids may also be denatured by an extended treatment with alcohol and Pauli * has found that even salts and acid will work the change in time. Alcohol at first precipitates a soluble variety of proteid, which becomes insoluble on long standing.

Behavior of Globulins

As already pointed out globulins have the property of being soluble in dilute salt solutions but not in pure water. Excess of salt precipitates them, but they will redissolve when the dilution is increased sufficiently. These peculiarities are due to the chemical composition of the substances. Hardy,† who has carefully studied the solubility relations, regards globulin as a substance insoluble in water, but which unites with alkali salts to form soluble complex salts, the reaction being similar to the dissolution of silver chloride by ammonia. He believed that globulin and NaCl formed a complex, NaGlob . Cl, the amount naturally depending upon the concentration of the NaCl. This complex could dissociate thus:

$$\text{ClGlob. Na} \rightleftharpoons \text{ClGlob.}^- + \text{Na}^+.$$

The dissociation would be dependent upon the concentration of the NaCl, and at great dilution the complex ion would be completely dissociated and the globulin would therefore be insoluble.

$$\text{ClGlob. Na} = \text{Na}^+ + \text{Cl}^- + \text{Globulin (insoluble)}.$$

At moderate concentrations of the NaCl a part of the proteid is dissolved in the form of an electrolyte, while the remainder is present as submicrons. At high concentrations of the salt the dissociation is so far driven back that precipitation occurs. The experimental results of Michaelis ‡ with the ultramicroscope are in accord with this point of view. He observed that globulin solutions diluted with water contain a much larger number of submicrons than those at the same dilution when salt was present. However the colloidal solutions are stable which is most easily explained on the assumption that the ultramicrons have adsorbed globulin-chloride ion according to some such reaction as the following:

$$\boxed{\text{U}} + \text{ClGlob.}^- \rightleftharpoons \boxed{\text{U}}\ \text{ClGlob.}^-$$

Hardy§ has also investigated the union of globulin with acids and bases. He assumed the formation of globulin ion that would be

* W. Pauli und H. Handovsky: Hofmeisters Beiträge z. chem. Physiol. u. Pathol., **5**, 27–55 (1903).

† W. B. Hardy: Journ. of Physiol., **33**, 251–337 (1905); Proc. Roy. Soc., **79** (B.), 413–426 (1907).

‡ L. Michaelis: Virchows Archiv. f. pathol. Anat. u. Physiol., **179**, 195–208 (1905).

§ Hardy: *l. c.*

affected by hydrolysis. Naturally the globulin salts of weak acids would hydrolyze to a greater degree than those of strong acids, and therefore the formation of ultramicrons would be favored in the former case.

Ultramicrons formed from globulin salts are doubtless charged by the adsorption of ions in a manner similar to that just indicated. It is interesting that the charged ultramicrons have a greater mobility under the influence of a potential fall than the ordinary proteid ion. Hardy discriminates between true ions and pseudo-ions. The latter are charged ultramicrons.

3. Special Examples

A. Gelatins, Their Preparation, and Properties

Colorless purified glue or glutin is known as gelatin. Glue is made by boiling collagen in water to which acid has been added. The chemical composition is approximately as follows:

	Per cent.
C	49 to 50
H	6.4 to 6.7
N	17.8 to 17.9
S	0.2 to 0.7
O	24 to 25

The large variations in the sulfur content would indicate that a substance rich in sulfur is present as an impurity.

Decomposition Products. — Among the products of decomposition are amino-acids, such as glycocoll, leucin, asparaginic and glutaminic acids, alanin, phenylalanin, α-prolin, etc. Tyrosin is not present.

Reactions. — In general glue is not precipitated at boiling heat by acids, alum, white lead, or other salts of the metals. It is precipitated by tannic acid in the presence of salts and by $HgCl_2$ in the presence of NaCl and HCl. On boiling glue goes over into a modification β glutin that cannot be coagulated. On long boiling especially in the presence of acids, glue albumoses and glue peptones are formed, and out of these by further splitting amino-acids are obtained.

Protective Effect. — Gelatins possess an extraordinary protective effect, and are in this regard scarcely surpassed by any other material. At boiling heat the gold number is 0.005 to 0.01.* At lower temperatures, *i.e.*, 80 degrees, the subdivision is not so great and the solutions have a somewhat smaller gold number. Still higher gold numbers can be obtained if gelatin solutions having a concentration of 0.1 to 1 per cent are allowed to stand over night and are diluted to $\frac{1}{100}$ per cent on

* W. Menz: Zeit. f. phys. Chemie, **66**, 129–137 (1909).

the following day. The more concentrated the solution the greater the size of the submicrons and therefore the smaller the protective effect.

Osmotic Pressure of Gelatin Solutions. — The determination of the osmotic pressure has revealed pronounced hysteresis phenomena as shown by Lillie.* Moore and Roaf.† observed a greater increase in the osmotic pressure with a rise in temperature than corresponds to the same rise in solutions of crystalloids. On cooling, the original pressure is not obtained for some time, but remains considerably above the normal. Lillie kept a gelatin solution in the ice chest for two days and then heated a part of the solution for three hours at 65 to 70 degrees. Both solutions were brought to the temperature of the room and the pressure measured. The solution that had been warmed showed a greater pressure than the other but after a time both columns stood at the same height. The equilibrium was reached in the solution that had been warmed much sooner than in the other. The observation is in good agreement with the general behavior of the two solutions. At first the one that had been warmed contained much smaller particles, thus accounting for the greater pressure. After standing some time the degree of dispersion in both solutions became the same.

Graham considered glue a typical colloid because it was so easy to obtain both the solution and the gel. As is well known glue distends in water to form a gel, and on warming a thick liquid is obtained. On cooling the solution becomes a more or less stiff gel. The reaction is reversible as long as the heating is not kept up for too great a length of time, in which case chemical reactions set in. Changes in the viscosity, elasticity, and in the addition of other substances have been thoroughly studied. Of special interest is the phenomenon of gelatinization itself.

Ultramicroscopy of Gelatin Solutions and Gels. — Pure warm gelatin solutions appear to be almost homogeneous. On cooling there is formed, according to the concentration, an amicroscopical or a submicroscopical heterogeneity. The maximum size of the particles is reached in 0.5 to 1 per cent solutions, which harden to porous gels. The farther the concentration decreases from 0.5 per cent the smaller the visible particles become, and the more mobile the liquid. The greater the concentrations over 0.5 per cent the more rigid the gels formed on cooling. Submicrons may be observed in solutions from 0.1 to 6 per cent. At concentrations greater than 6 per cent or less than 0.1 per cent only amicrons are present.

* R. S. Lillie: Amer. Journ. of Physiol., **20,** 127–169 (1907).

† B. Moore and H. E. Roaf: Biochemical Journ., **2,** 34 (1906).

If warm gelatin solutions are considered homogeneous, cooling causes the appearance of a new phase, and the process is similar to that of crystallization where the crystals are of ultramicroscopical dimensions, *i.e.*, the preparation of colloidal gold, silver, salts,* etc. It is also similar to a liquid at the critical point. Weimarn has observed that, similar to gelatin, during the formation of crystalline precipitates, the size of the particles is at a maximum at moderate concentrations and that at higher concentrations the precipitate is a gel. These observations are scarcely comparable to the hardening of gelatin because in the latter case the medium is always water, while crystalline precipitates are formed in electrolytic solutions, where the concentration is constantly varying. This, of course, has an effect on the size of the particles. The difference between gelatin solutions and crystallization, or solutions at the critical point, is that in the first case microns, submicrons, ultramicrons, or amicrons are formed according to the concentration. It should also be noted that during the cooling of gelatin solutions visible particles made up of smaller amicrons are present. The appearance of visible particles is therefore not dependent upon the formation of a gel that hangs together. The closer the particles are together the greater will be the viscosity of the solution. When the particles are close enough they hold together and form a gel, that contains a great deal of the liquid which may be pressed out.

The structure of gelatin gels has been studied a great deal microscopically. As the ordinary gel from aqueous solution appears to be homogeneous Bütschli and also Hardy § have endeavored to make the structure visible. The latter investigator allowed gelatin hydrosols containing alcohol to harden and viewed the process under the microscope. In dilute solutions drops separated out on cooling that united with each other to form a net-like structure. This net was surrounded by a phase that contained less gelatin. In the case of more concentrated solutions an enclosed phase richer in gelatin was formed which contained drops of the water alcohol solution. Bütschli ‡ made the structure visible in concentrated gels by treating them with alcohol or chromic acid, etc.

Pauli § has shown that gelatin is materially changed by such treatment and the structure must therefore be considered artificial. It has since been shown that gels treated with these reagents have different

* P. P. v. Weimarn: Koll.-Zeit., **2–3**.

† W. B. Hardy: Zeit. f. phys. Chemie, **33**, 326–343 (1900).

‡ O. Bütschli: Untersuchungen über mikroskopische Schäume und das Protoplasma. Leipzig (1892).

§ W. Pauli: Der kolloidale Zustand und die Vorgänge in der lebendigen Substanz. Braunschweig (1902). Naturwiss. Rundschau, **17**, Nr. 25, 26, 27 (1902).

properties from the gels obtained from pure water. Hardy's alcohol gels, for instance, are less consistent and are somewhat milky. At the suggestion of the author, Bachmann has repeated the experiments of Bütschli and Hardy, and found that there is a marked difference between the structure of water gels and those treated afterward by alcohol or chromic acid. The former are much finer. In fact gels having a concentration of over 6 per cent allow no differentiation of the particles even under the cardiod ultramicroscope with sunlight. That there is a very fine discontinuity is revealed by the fact that the Tyndall effect is apparent. The refracted light suffers linear polarization.

According to the explanation given by Bachmann * the structure of the gels obtained by Bütschli is due to a conglomeration of particles forming denser units that are separated by capillary spaces large enough to be seen under an ordinary microscope. A distinct structure is visible under the ultramicroscope in the case of gels from solutions of 0.5 to 1 per cent. Flocks of microns or submicrons may be distinguished.† These accumulations have different shapes, and the flocks must be regarded as groups of amicrons.

The formation of the gel itself under the ultramicroscope is interesting and has been studied by Menz,‡ v. Weimarn,§ and Bachmann.* If a 0.5 per cent solution is allowed to cool a multitude of submicrons can be detected, which grow by joining together to form flocks. The particles are not at rest but have a vibratory motion not quite so great as they have in the hydrosol. Gradually the solidity increases and the motion becomes less and less. The rate of solidification may be regulated by judicious cooling. The process has a certain similarity to the separation at the critical points of liquids. At the suggestion of the author v. Lepkowski ¶ investigated the critical phenomena under the ultramicroscope. During the cooling an intense lighting up of the field is observed shortly before the separation, and multitudes of not clearly defined submicrons are present. Suddenly a new phase appears in the form of tiny drops. On warming a motion on the surface of these drops can be seen and they either become invisibly small, or the contours gradually fade and the place where the drops were is now characterized for some little time by a glimmering zone. Evidence of

* W. Bachmann: Inaug.-Diss. Göttingen (1911); Zeit. f. anorg. Chemie, **73**, 125 172 (1911).

† P. v. Weimarn: Koll.-Zeit., **10**, 132 (1912).

‡ Menz: *l. c.*

§ P. v. Weimarn: Koll.-Zeit., **4**, 133 (1909); **6**, 277 (1910). Grundzüge der Dispersoidchemie. Dresden (1911).

¶ W. v. Lepkowski: Zeit. f. phys. Chemie, **75**, 608–614 (1911).

the small diffusion in the liquid is afforded by the fact that on cooling the drops may be obtained on the spot where they disappeared. In fact two particles that were prevented from uniting by the warming may be so far restored that they will unite after the cooling process has been carried out. In contradistinction to the case of gelatin submicrons from critical systems unite to form a homogeneous phase even after the cooling. The drops are circular, large, and have no such variations in form as are so prominent in the case of gelatin particles.

In regard to the above observations on gelatin under the ultramicroscope it must be borne in mind that the finest structure seen is not by any means the finest present in the system. The resolving power of the ultramicroscope is such that if two particles are closer together than one-half the wave length, the two would appear to be one particle. How conclusions may be made with regard to finer structures than this, has been discussed under the heading, Gels of Silicic Acid.*

Gelatinization and Distention † (Swelling)

Gelatinization and distention have been the subjects of many physical investigations. Changes in viscosity, elasticity, the heat of reaction during distention, and the influence of additions on the temperature of gelatinization have also been carefully studied.

Distention. — In water gelatin distends to form a gel, and takes up 8 to 10 times its weight of water. Most of this water is given up again in an atmosphere saturated with water vapor, and equilibrium is again established when the water is about 50 per cent of the weight of the dry gelatin. This water is much more firmly bound than that actually necessary for distention, and is given up but slowly under reduced aqueous vapor pressure. This is determined by the heat of reaction during distention, and by the rate of distention. According to Wiedemann and Lüdeking ‡ the heat of distention is 5.7 cals. per gram of dried gelatin. On the contrary during the liquefaction of gelatin heat is taken up. The process is comparable to the dissolution of many salts whereby heat is at first given out owing to the formation of hydrates, but afterwards heat is taken up as the dilution is continued. The heat of distention depends upon the degree of moisture in the hydrogel. This is shown by table 39 taken from Rodewald's§ investigations. After the amount of water has risen to about 20 per cent not much

* P. Böhi: Inaug.-Diss., 27. Zürich (1911).

† Journ. Am. Chem. Soc., **37**, 1295.

‡ E. Wiedemann und Ch. Lüdeking: Wiedemanns Annalen d. Phys. u. Chem. N. F., **25**, 145–153 (1885).

§ H. Rodewald: Zeit. f. phys. Chemie, **24**, 206 (1897).

more heat is given out. Hand in hand with a large heat of distention goes a large contraction, particularly in the first stages. The researches of Hofmeister,* and of Pascheles † on the rate of distention indicate that the water at first added is firmly bound. The water is taken up rapidly at first and then more slowly toward the end.

TABLE 39

% H_2O.	Q.
0.23	28.11
3.23	20.97
8.16	12.43
12.97	7.37
19.52	2.91

Solidity. — Dried glue is characterized by an extraordinary firmness. This is exemplified by the strength glue exhibits in holding two pieces of wood or glass together. In the latter case the glass is often torn at the surface before the two pieces can be forced apart. Reliefs in glass surfaces are made in the industries by this method. The experiment shows the enormous adhesion between glue and other amorphous substances. The firmness decreases with increasing water content.

On freezing moist gelatin suffers a change of state, and after the thawing the properties are somewhat different. This is apparent in the structure under the microscope, in the decrease of adhesive power, and also in decreased distention; see page 64.

That a considerable portion of the water in gelatin gels is weakly bound is shown by the researches of Bütschli.‡ The gel was rubbed into a paste, put into an unglazed porcelain cell and the latter subjected to reduced pressure by a water pump. In this manner he was able to remove all but 25 per cent of the water when gels of 5 to 10 per cent concentration were employed. Even when the warm solution was poured into the cell and allowed to solidify the water could be withdrawn by the same process. It could not be carried out, however, when the concentration was 20 per cent. This agrees very well with the property that gels from dilute solutions often have of contracting and giving up a part of the water contained, and also with the observation that distended gelatin will give up a portion of its water even in an atmosphere saturated with water vapor.

* F. Hofmeister: Archiv. f. experim. Pathol. u. Pharmakol., **27**, 395–413 (1890).
† W. Pascheles (Pauli): Pflügers Archiv. f. d. ges. Physiol., **67**, 219–239 (1897).
‡ O. Bütschli: Über den Bau quellbarer Körper. Göttingen, 22–26 (1896).

The Displacement of Water by Other Liquids. — Bütschli found that it was very easy to replace water in a gelatin gel with alcohol, and this again by chloroform, turpentine or xylol (xylene). In this manner gels are obtained that are turbid, solid, and do not shrink a great deal on drying. They are porous, chalk white and opaque. This is similar to an experiment carried out by Graham on silicic acid gels, and shows a close relation between gelatin gels and those purely inorganic, although the latter may have a somewhat finer structure. The investigation of the vapor tension curves during the drying would doubtless give valuable information about the size of the enclosed spaces.

The Distention of Gelatin and Other Colloids in the Presence of Electrolytes. — Through the investigations of Hofmeister,* Pauli,† Spiro,‡ W. Ostwald,§ and Fischer, the distention of gelatin in the presence of electroytes has become well known. The last-named author has shown that not only gelatin but also fibrin, muscle and the substance in the eyes of cattle behave similarly. He has also discovered a relation between the distention in colloids and the abnormal accumulation of water in animal fibers.

From the work of Spiro we learn that acid and alkalis have a much more pronounced distending effect than water. Wo. Ostwald has shown that acids vary in their effectiveness. The following series is arranged in descending order of the effectiveness.

Hydrochloric acid > nitric acid > acetic acid > sulfuric acid > boracic acid.

Fischer has shown that the acid and alkali distention of gelatin, fibrin, muscles and the substance in the eyes of animals is depressed by the presence of salts. Chlorides, bromides and nitrates have a much less depressing effect than acetates, sulfates or citrates. This series agrees in the main but not completely with that obtained in the precipitation of proteids. According to Fischer ¶ the abnormal accumulation of water in the tissues is not caused by differences in blood pressure, but by acids formed in the tissues, either because of disturbances in the circulation, or by infections.

* F. Hofmeister: Archiv. f. experim. Pathol. u. Pharmakol., **27**, 395–413 (1890); **28**, 210–238 (1891).

† W. Pauli: Pflügers Archiv. f. d. ges. Physiol., **67**, 219–239 (1897); **71**, 333–356 (1898).

‡ K. Spiro: Hofmeisters Beiträge z. chem. Physiol. u. Pathol., **5**, 276–296 (1904).

§ Wo. Ostwald: Pflügers Archiv. f. d. ges. Physiol., **108**, 563–589 (1905); **111**, 581–606 (1906).

¶ M. H. Fischer: Œdema. New York (1910).

If gelatin is pricked with a needle that has been previously dipped in formic acid and the entire mass covered with water, those places that have been pricked will distend much faster than the others. The swollen places resemble swellings on the human skin caused by the sting of insects. Just as sulfates, acetates and especially citrates may be used to reduce the distention of gelatin so may they be employed to reduce the accumulations of water in the tissues.

Diffusion Through Gelatin, Ultrafiltration

Graham * and other investigators have found that gels offer very little resistance to the passage of electrolytes. Nell,† Bechhold and Ziegler ‡ have recently shown that only dilute gels offer a negligible resistance, while concentrated, on the contrary, show considerable. This is quite in accordance with the knowledge obtained through the ultramicroscope that the structure of gels is granular. Little resistance is offered by the large spaces in a thin gel to the passage of electrolytes. A more concentrated gel would entail the passage of the molecules through the walls made of gelatin, and thus cause a greater resistance.

Colloids in general do not diffuse through gels. The retarded diffusion is probably connected with adsorption. Thick collodion membranes generally effectually prevent the passage of ultramicrons. Diffusion is usually very complicated in gels where the size of the pores, ultramicrons, adsorption, charge and discharge of the particles all play a part. Liesegang§ has devised a very pretty experiment in the diffusion of silver nitrate through gels containing chromium. A system of rings is formed around the drops of silver nitrate, where the distance of the rings from the drops increases with the progress of the diffusion. Ostwald ¶ has offered an explanation for this, but Bechhold,|| and Liesegang ** contend that the process is more complicated. Bechhold †† and Ziegler allowed salts that would give a precipitate to diffuse against each other, and observed that the precipitate often completely obstructed the diffusion. By melting the jelly the process progressed further.

Ultrafiltration by Gelatin. — Bechhold ‡‡ observed that hardened gelatin allowed solutions of crystalloids to pass through unobstructed,

* Th. Graham: Liebigs Annalen, **121,** 5, 29 (1862).
† P. Nell: Annalen d. Phys. (4), **18,** 323–347 (1905).
‡ H. Bechhold und J. Ziegler: Zeit. f. phys. Chemie, **56,** 105–121 (1906).
§ R. Liesegang: Liesegangs photogr. Archiv., 321–326 (1896). Chemische Reaktionen in Gallerten. Dusseldorf (1898).
¶ W. Ostwald: Lehr. d. allg. Chemie (2 Aufl.), **2,** 11, 778 ff.
|| H. Bechhold: Zeit. f. phys. Chemie, **52,** 185–199 (1905).
** R. Liesegang: Zeit. f. phys. Chemie, **59,** 444–447 (1907).
†† H. Bechhold und J. Zeigler: Annalen d. Phys. (4), **20,** 900–918 (1906).
‡‡ H. Bechhold: Zeit. f. phys. Chemie, **60,** 257–318 (1907).

but held back colloidal particles, just as collodion filters do. These facts indicate a granular or at least an open net structure of the gelatin, the walls of which offer a great resistance to the filtration. Beside the considerations discussed under diffusion, other factors must act. According to Bechhold * the pores of his filter were much larger than the ultramicrons that they held back. It is not impossible that the impermeability of the filter for colloids is connected with a dynamic process on the surface, and that the kinetic theory may throw some light on the phenomenon.

B. Hemoglobin

Hemoglobin and Oxyhemoglobin

The red color of the blood is occasioned partly by the presence of hemoglobin, a protein body, and partly by oxyhemoglobin, a compound of oxygen and hemoglobin. In the red corpuscles the hemoglobin is surrounded by another substance, and perhaps also by a membrane. The material of this substance is composed largely of the so-called lipoids, chloresterin, lecithin, etc. The liquid in the red corpuscles is isotonic with a sodium chloride solution having a concentration of 9 parts per million. In this latter solution the corpuscles remain unchanged, while in one more concentrated they shrink, or swell in one more dilute. This distention may proceed so far that the hemoglobin separates out from the other liquid in the corpuscles and goes into the outer solution. This process is known as hemolysis. Freezing and the influence of some reagents, such as ether, chloroform, saponin, may also cause hemolysis.

Hemoglobin dissolved in water will not diffuse through membranes, and the solution, according to the definition of Graham, is colloidal.† It is also worthy of note that Bechhold's filter of suitable thickness will prevent the diffusion of the hemoglobin. In fact Bechhold employs this means of determining the permeability of his membranes.

Hemoglobin crystals from the blood of different animals do not have the same composition nor properties. Bohr assumes that there are different sorts of hemoglobin in the blood of a single species, but according to Hüfner there is only one hemoglobin in the blood of cattle. Noteworthy is the iron content, which is connected with the taking up of oxygen by the hemoglobin. Indeed this property of hemoglobin to take up oxygen, carbon monoxide, and other gases is of highest importance to form oxyhemoglobin, or carbon monoxide — hemoglobin. Hüfner ‡ has found that 1 mol. of hemoglobin will take

* H. Bechhold: Zeit. f. phys. Chemie, **64**, 328–342 (1908).

† J. Lemanissier: Etudes des corps ultramiscroscopiques. Paris (1906).

‡ C. Bohr: Centralbl. f. Physiol., **4**, 249–252 (1890).

up 1 mol. oxygen at higher pressures; or 1 mol. oxygen is taken up for every mol. iron in the hemoglobin.

Oxyhemoglobin crystallizes much more easily than hemoglobin and may be prepared in the following way.

Well-washed blood from dogs or horses is added to 2 volumes of water and shaken with ether. The excess of ether is poured off and the amount dissolved allowed to evaporate in a shallow dish at 0° C. The liquid is allowed to stand for two to three days after about one-fourth volume of alcohol has been added. The product is purified by recrystallization from aqueous solution by the addition of alcohol. The crystals have about the following composition.

	Per cent
C	53.8 to 54.7
H	6.9 to 7.3
N	16 to 17.5
S	0.4 to 0.6
O	19 to 22
Fe	0.33

The absorption spectrum of oxyhemoglobin is markedly different from that of hemoglobin. The former has two sharp well-defined absorption bands between *D* and *E*, while the latter has only one. Such differences in the absorption spectra cannot be explained on the grounds of a difference in state, nor in the degree of dispersion of the hemoglobin. Rather it indicates a change in the chemical composition of the two substances.

Oxyhemoglobin will give up its oxygen very easily; is easily reduced in other words, and this fact is of great importance in the oxidation processes in the body. Oxygen is taken up in the lungs and transported to the tissues where the oxidation processes go on. Numbers of measurements have been made on the amount of oxygen taken up by the blood without any very great agreement among the different experimenters. It would seem that carefully prepared solutions of hemoglobin might lead to more satisfactory results; because in the blood, which is a mixture of several protein bodies, adsorption of the oxygen in the disperse phase must play a part as well as chemical combination. Ostwald * has shown that the adsorption isotherms are suitable for describing the quantitative adsorption of the oxygen.

Methemoglobin. — On long standing and also under the influence of a series of different reagents oxyhemoglobin goes over into another modification, known as methemoglobin. Oxidizing and reducing agents, as well as many indifferent substances, effect or accelerate the change. The transition was previously regarded as a reduction, but

* Wo. Ostwald: Koll.-Zeit., 2, 264–272, 294–301 (1908).

Hüfner * has demonstrated it to be an oxidation process. The product is much more stable than oxyhemoglobin, does not give up its oxygen in vacuum, and may be crystallized like oxyhemoglobin. Methemoglobin has a different absorption spectrum in acid and alkaline solution. Both of these are different from that of oxyhemoglobin. According to Kühne † and Preyer ‡ oxyhemoglobin and methemoglobin are acids, while hemoglobin is not. Oxyhemoglobin is much more insoluble than hemoglobin. These differences indicate quite clearly that oxyhemoglobin is chemically different from hemoglobin, and that the former is not merely an adsorption compound of oxygen with the latter.

Carbon Monoxide-Hemoglobin. — As in the case of oxygen hemoglobin forms a compound with carbon monoxide, whereby the color becomes cherry red. The crystals of this substance show a weak but beautiful pleochroism, purple, red and white. The absorption bands are similar to those of oxyhemoglobin, but are displaced somewhat more toward *E*. Carbon monoxide is given up with difficulty, and this accounts for the fact that carbon monoxide can displace oxygen in the blood even when the latter gas is present in moderate concentration, hence the poisonous effects of carbon monoxide in the blood. Twenty-seven per cent of the hemoglobin will be united to carbon monoxide when the latter is present in the air at a concentration of only 0.05 per cent, and the partial pressure of the oxygen is 545 times greater than that of the carbon monoxide. Carbon monoxide-hemoglobin is much more difficult to turn into methemoglobin. It is also much more stable toward reagents than oxyhemoglobin. Many substances that change oxyhemoglobin into methemoglobin do not affect carbon monoxide-hemoglobin.

Molecular Weight of Hemoglobin

Hüfner § has shown that 1 gram hemoglobin unites with 1.338 cc. carbon monoxide (= 0.00167 g.) at normal conditions. On the assumption that the combination takes place in molecular amounts of each, the molecular weight of hemoglobin would be 16,721. The iron content of the blood is 0.336 per cent. On the assumption that one molecule of hemoglobin contains one atom of iron the molecular weight would be 16,666, practically the same value as that obtained

* G. Hüfner und J. Otto: Zeit. f. physiol. Chemie, **7,** 65–70 (1882). Ders. und R. Külz: *Ibid.*, **7,** 366–374 (1883).

† W. Kühne: Virchows Archiv., 34, 423–436 (1865).

‡ W. Preyer: Centralbl. f. d. med. Wiss., 273–275 (1867); Pflügers Archiv. f. d. ges. Physiol., **1,** 395–454 (1868).

§ G. Hüfner: Englemanns Archiv. f. Physiol., Physiol. Abt., 130–176 (1894); 217–224 (1903).

on the basis of the taking up of carbon monoxide. It is quite possible that one molecule of hemoglobin contains more iron than we have assumed, *i.e.*, *n* molecules of iron. Hemoglobin would therefore take up *n* mols carbon monoxide to one hemoglobin, and have a molecular weight *n* times the above number. In order to decide this question Hüfner and Gansser * measured the osmotic pressure of a hemoglobin solution with the help of a parchment bag employed by Schleicher and Schull. Fig. 33 represents the apparatus.

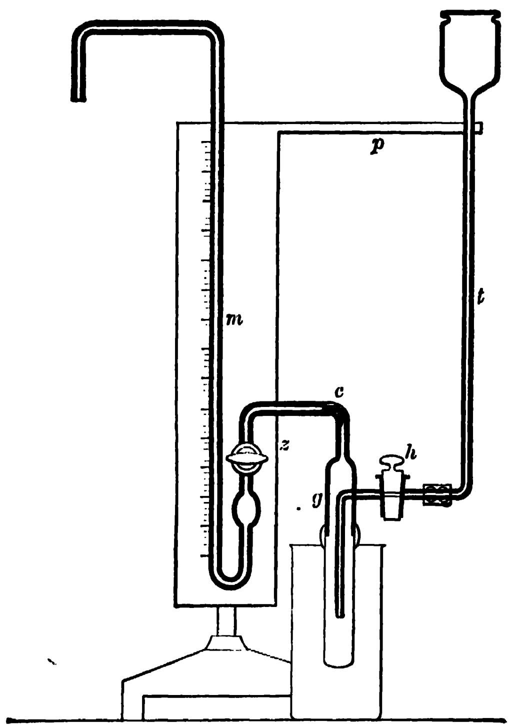


FIG. 33. Hüfner's apparatus for the determination of osmotic pressure.

A parchment bag, 100 mm. long and 16 mm. wide is connected with the manometer by means of the capillary tube, *c*. A funnel tube, *t*, is held in place by the arm of the ring stand, *p*. The capillary under the two-way stop cock, *z*, has a small bulb of about 1 cc. capacity. The bag is softened with water, securely bound on the glass tube, *g*, and covered with a thick layer of picene by melting it over a burner. The manometer is filled by suction at *z*. The bag is filled with hemoglobin through the funnel and the liquid is allowed to flow out at *z*.

* G. Hüfner und E. Gansser: Engelmanns Archiv. f. Physiol., Physiol. Abt., 209–216 (1907).

z is now opened to the manometer and h is closed. The beaker is filled with water and the apparatus allowed to stand. In 18 to 24 hours the mercury will have risen to its maximum. The volume, however, has increased by osmosis and it is necessary to multiply by $\frac{v'}{v}$ in order to get the proper pressure. The molecular weight may be calculated by the formula

$$M = \frac{22.41\,(1 + 0.00366\,t)\,0.760\,c}{p'},$$

where c is the amount of substance dissolved in a liter, and p' is the corrected pressure in millimeters of mercury. For further details reference must be made to the original article.

The average of four determinations in the case of the blood of horses gave a molecular weight of 15,115, while the average of ten determinations with the blood of cattle gave 16,321. In the last case the minimum and maximum were 15,500 and 18,370 respectively.

Size of the Hemoglobin Molecule

The agreement of the molecular weight found with that calculated from chemical data is remarkable. We have here an excellent example for showing how the same point may be arrived at by two entirely different methods.

Because of its behavior toward dialysis and ultrafiltration hemoglobin in solution must be considered a colloid. On the other hand, the ease with which oxyhemoglobin can be crystallized would place these substances with the crystolloids. All methods give a molecular weight of over 16,000 for hemoglobin from the blood of cattle. But these enormous molecules will not diffuse through membranes, and Bechhold has shown that they can be filtered off by means of collodion filters made in glacial acetic acid. We are, therefore, led to the conclusion that the molecule of oxyhemoglobin and the ultramicron is one and the same particle. Similar cases are presented in the dyestuff domain, but because of electrolytic dissociation the determined and the calculated molecular weight do not agree so well as in the case under discussion.

Reinganum * has submitted the following formula for the determination of the diameter of the molecules.

$$\delta = 0.882 \cdot 10^{-8} \sqrt[3]{\frac{M}{S}}\,\text{cm}.$$

* See R. Lorenz: Zeit. f. phys. Chemie, **73**, 253 (1910).

Here M is the molecular weight, S the specific gravity at boiling temperature, $\frac{M}{S}$ is the molecular volume that can be approximately calculated from Kopp's rule. Under the assumption that the formula given for the hemoglobin in the blood of the dog by Jaquet is correct,

$$C_{758}H_{1203}N_{195}O_{218}FeS_3,$$

the diameter of the hemoglobin molecule would be

$$2.3 - 2.5\ \mu\mu,$$

according to whether we take Kopp's lowest or highest value for the atomic volumes of O and N.

It is worthy of note that the determinations of the diameter of amicrons in gold solutions have given values similar to the above.* In other words there is no great difference between the room taken up by the gold amicrons and the molecules of hemoglobin. Gold particles may be either larger or smaller than the molecules of hemoglobin.

C. Casein

Casein belongs to the true protein bodies, and specifically to the group of phosphorglobulins. By pepsin digestion these give pseudonuclein a substance that contains phosphorus. Pseudonuclein becomes dissolved by further digestion and differs from the nuclein of the nucleoproteids in its decomposition products. The phosphorglobins were previously classed with the nucleoproteids, but the phosphorus content is about the only thing these two groups have in common. The phosphorglobulins have also nothing to do with the cell nucleus out of which the nucleoproteids are obtained.

Casein is the most important protein body in milk. Besides its chief function as nitrogenous food it plays the important role of protective colloid for the fat particles and also for calcium phosphate with which it forms a colloidal combination. It keeps the fat particles in a fine state of emulsion and prevents them from uniting into clots, probably due to the formation of a fine membrane around the particle. Casein may be precipitated from milk by acids. It is insoluble in water and also in the solutions of neutral salts, except sodium fluoride and potassium oxalate. Casein has acid properties, drives carbon dioxide out of carbonates, and is soluble in alkalis. The ammoniacal solution possesses a high protective effect toward colloidal gold. The gold number 0.01 indicates that it belongs therefore to the protective colloids of the first class. The behavior toward bases has been care-

* R. Zsigmondy: Zeit. f. phys. Chem., **56**, 65–76 (1906).

fully investigated by Laqueur and Sackur,* and also by Robertson.† The two former concluded from their work that the proteid ion is responsible for the increased viscosity of proteid solutions.

Pure casein solutions do not curdle on boiling. Acids do not cause complete precipitation unless the temperature is raised to the boiling point. A slight excess of calcium hydroxide also causes turbidity and coagulation on warming. The turbid accumulation dissolves again when the temperature is lowered. Concentrated solutions of calcium and casein become covered with a film on boiling just as milk does.

Acid and Rennet Coagulation. — Acetic and mineral acids precipitate casein. The precipitate dissolves again in an excess of the acid, and this behavior is in accordance with the amphoteric character of casein as a member of the proteid group of substances. Rennet, an enzyme from the stomach of a calf, causes another sort of coagulation in casein solutions containing calcium. This is of industrial importance in the making of cheese. Calcium-free casein solutions are not precipitated by rennet. That it causes a change to take place, however, is manifested by the fact that calcium ion added afterward causes immediate precipitation.

Occurrence in Milk. — Casein calcium, or a colloidal combination of casein and calcium phosphate, is present in milk in the form of submicrons. They are there in enormous numbers; cow's milk contains 3 to 6 billions per cubic centimeter. Under the assumption of cubical form and a complete filling of the space the linear dimensions would be 130 to 170 $\mu\mu$. The particles are therefore fairly large and can be seen with artificial light. The size of the particles agrees with the experimental fact that they may be retained by unglazed porcelain filters, and casein can be separated from milk by this means. Wiegner ‡ has shown that the number of submicrons in cow's milk is remarkably constant. Human milk is easily distinguished from that of the cow because the number of submicrons visible under the ultramicroscope is much greater in the latter.

If it is necessary to prevent the precipitation or coagulation of casein by acids a protective colloid stable against acids must be added, such as gelatin, or albumin. According to J. Alexander § these additions are necessary in the preparation of ice cream. If the protective colloid

* E. Laqueur und O. Sackur: Hofmeisters Beiträge z. chem. Physiol. u. Pathol. **3,** 193–224 (1903).

† T. B. Robertson: Journ. of Physic. Chemistry, **11,** 542–552 (1907); **12,** 473–483 (1908).

‡ G. Wiegner: Koll.-Zeit., **8,** 227–232 (1911).

§ Jerome Alexander: Journ. of Soc. of Chem. Industry, **28,** 280 (1909); Journ. of Amer. Med. Assoc., **55,** 1196–1198 (1910).

is not added the ice cream becomes somewhat granular and not quite so pleasant to the taste.

Another interesting point raised by this same author is that of the comparison of human and cow's milk for children. The cow's milk is usually diluted with water and the necessary amount of milk sugar added. This is, however, not sufficient to render the milk similar in content to that of the human species. A striking difference between the two sorts is illustrated by the fact that human milk is not so easily coagulated by acids as cow's milk. The latter contains more casein and less albumin as will be seen from the following table.

TABLE 40

Constituents.	Human milk.	Cow's milk.
Water	88.20	87.10
Proteins { Casein	0.75	3.02
Proteins { Albumin	1.00	0.53
Fat	3.50	3.69
Sugar	6.20	4.88
Ash	0.25	....

The albumin acts as a protective colloid for the casein and this explains the different behavior of the two substances. Several American medical men have realized this difference and favor the addition of protective colloids such as gum arabic, dextrin, etc., to cow's milk before giving it to children. Alexander has shown that cow's milk may be made to react much more like human milk if the protective colloids are added. Some authors have also claimed that casein from the two sources is not the same. This is probably due to the protective action of the albumin, because by dissolving the casein from human milk, and reprecipitating several times, it resembles more and more that from cow's milk.

PART II

INDUSTRIAL COLLOIDAL CHEMISTRY

PREFACE TO PART II

The chemistry of the colloidal state of matter has become of such great importance to the chemical industries that it has seemed wise to devote several chapters in this book to a side of the question that is particularly interesting to the technical chemist. As the subject is far too inexhaustible to be dealt with comprehensively in the space available it has been found necessary to omit any protracted discussion of the wide field of biological chemistry. It has also been found impossible to deal adequately with the colloidal chemistry of carbohydrates and organoplastics, owing to the fact that a great deal of the necessary information is unavailable in the literature.

ELLWOOD B. SPEAR.

CHAPTER XIII

INTRODUCTION TO PART II

From a practical point of view some of the most desirable properties of matter such as plasticity, elasticity, etc., are possessed in the highest degree by amorphous substances. As examples may be cited rubber, leather, cellulose, glue, organoplastics, and many others. While all amorphous substances are not colloidal in nature (some pure metals and their alloys for instance) most of them belong in the realm of colloidal chemistry. Hence many generalizations concerning the amorphous state are applicable to the colloidal. Some of these fundamental ideas have been emphasized by Lewis * in an article on the chemistry of amorphous solids. His basic idea in a somewhat modified form will be employed occasionally in the remaining chapters of this book.

Colloidal particles may be conceived to be built up of a relatively small unit *U* associated with itself by polymerization, condensation, adsorption or otherwise, *n* times. A single particle would therefore be represented by the formula *Un*. It is not necessary at this point to make any assumption as to the nature of the association. It may be chemical or physical, or both.

U may be a single molecule of the substance in question as in the case of colloidal gold or other metals; or it may be the union of several smaller units U_1, U_2 of different substances as in the case of gelatin, which is a condensation product of several amino acids; finally it may be a group that is represented by the simplest possible formula under the circumstances. As instances may be cited rubber C_5H_8, or cellulose $C_6H_{10}O_5$. The formulas for rubber and cellulose would therefore be $(C_5H_8)n$ and $(C_6H_{10}O_5)n$ respectively, where *n* may or may not have the same value in the two instances. *N* is a pure number and may have many different values in the same colloidal substance where the particles differ in size.

The point of view as outlined above gives a somewhat clearer conception of many phenomena met with in colloidal chemistry. For instance we are now able to distinguish between two different kinds of coagulation. The tiny droplets of oil in oil emulsions on separating from the water flow together to form a continuous phase oil, in which case *n* becomes 1 if oil exists in the liquid state as molecules. On the other hand it is

* Jour. Soc. Chem. Ind., **35**, 12 (1916).

probable that in the case of colloidal suspensions of metals the particles do not flow together during coagulation, but on the contrary larger entities are formed by surface contact of the smaller particles. The latter process could be represented thus: $Un' + Un'' \ldots = Un'\,Un'' \ldots$ where $Un'\,Un'' \ldots$ is an individual in a granular precipitate.

Between these two extremes, liquid particles suspended in a medium, on the one hand, and solid particles on the other, all possible grades exist. For instance colloidal ferric hydroxide, highly dispersed, has many properties of liquids in a similar condition. When it is coagulated, however, the resulting flocks cannot be considered a pure liquid. In fact it is better to call this and other solids not having a crystalline structure, supercooled liquids.

Gelatin solutions present a still more complicated system. As long as the gelatin is highly dispersed and the viscosity of the solution is low, because of the high temperature, the particles of the disperse phase, gelatin, may be represented by the formula Un. If the temperature is lowered and gelation takes place the water becomes the disperse phase, and the gelatin is continuous, or nearly so. Following out the scheme proposed, we could now say that the globules of water in the gelatin may be represented by the formulas Un', $Un'' \ldots$ where $U = H_2O$.

The fundamental difference between the growth of particles in Zsigmondy's nuclear solutions and true coagulation becomes clear from similar considerations. As long as gold is being reduced from a compound the molecules will be deposited upon the surface of the particles already present, and these particles will increase in size. In other words, the values of n', n'', . . . become greater. If a precipitating agent is now added the particles clot together by surface contact and form a granular precipitate.

The change of a reversible colloid to the irreversible state may be explained on the same basis. N may or may not be altered during the coagulation, but as soon as the changes in U are sufficiently fundamental the colloid becomes irreversible. A very good illustration is afforded by silicic acid, which becomes an irreversible colloid as soon as sufficient water is driven off to cause a change in the chemical composition of the silicic acid. Another very good example is that of caoutchouc and the finished product, rubber. Both of these substances are colloidal, but during vulcanization a fundamental alteration has taken place in U because sulfur has been introduced.

It should be noted in this connection that while the change in U in rubber is probably of a chemical nature, many instances are known in which the unit acquires very different properties, yet it is next to impossible to imagine that chemical reactions have taken place, *e.g.*, the addition of a small quantity of gelatin to a colloidal gold solution.

CHAPTER XIV

SMOKE, FLUE FUMES, LIQUID PARTICLES IN GASES

Solid and liquid particles ejected from cement plants, smelters, refiners, etc., have often been a source of direct loss to the companies, and have in many instances been so destructive to the surrounding property that a great deal of litigation, both on the part of private individuals and of the State, has resulted. Until recent years it was not recognized that the amelioration of these conditions involved problems of colloidal chemistry, but according to Wo. Ostwald's comprehensive classification on page (27) these systems fall under the heads 7 and 8, G + S (gas + solid) and G + L (gas + liquid).

The Smoke Nuisance. — The prevention of smoke in large cities, especially from locomotives and manufacturing establishments, has commanded considerable attention. Any apparatus capable of preventing smoke is too cumbersome for use on a locomotive. The most effective means is, of course, the electrification of the railways within the city limits; and it is safe to predict that the time will come when steam locomotives will not be employed for city transportation.

In the case of tall chimneys the problem generally resolves itself into one of scientific construction and stoking. It is obvious that if all the coal can be burned, in the firebox, or the dust recovered, pressed into briquettes and finally burned, the result is a net gain for the company, provided the cost of installation and the operating expenses are not too great. Where the latter is the case companies will naturally refuse to take preventive measures until obliged to do so by law. The plant necessary to eliminate the smoke nuisance is similar to that employed for the prevention of flue fumes from blast furnaces and smelters. It will be described under the next heading.

Flue Fumes. — The fumes from blast furnaces, roasters, converters, etc., consist of gases, mingled with liquid and solid particles, and are often of considerable economic value. Especially where sulfur dioxide, sulfur trioxide, copper, zinc and lead salts are ejected from the plant, the fumes are deleterious to the surrounding property; and many of these plants have been obliged by law to condense the larger portion of the fumes causing the damage. Moreover where the gases from blast furnaces are to be used for the production of power in internal

combustion engines, the larger dust particles must be eliminated. Several of the devices in operation will be briefly treated in this chapter, but only where distinct principles of colloidal chemistry are involved. For details of construction and of operation recourse must be had to works on metallurgy,* or to the original articles cited. The methods employed may be described as washing, centrifugalizing, settling, arresting, filtering, and electrical precipitation. In all these cases U is probably not materially altered. On the other hand, n may be increased very greatly, or possibly the particles may join together by surface contact to form irregular masses as suggested in the introduction to Part II.

Washing. — Washing the gases is usually accomplished by means of fine sprays, by bubbling through water, or churning in agitators. This method is employed for preparing gases of blast furnaces for use in internal combustion engines. The resulting liquid is very corrosive and soon affects the retainers. In short it is impractical for use in large plants where several hundred thousand cubic feet of gas per minute pass through at a temperature sometimes varying from 100 to 400° C.

Centrifugalizing. — Here the gases are either passed tangentially into a cylindrical, stationary container where the particles are thrown against the sides and fall down; or the gases are passed axially into a rapidly rotating cylindrical shell provided with baffle plates. The first of these methods is not efficient when the particles are very fine, and the second involves too much machinery for large volumes of gases.

Settling Chambers. — That dust particles will settle out of still gases better than they will from those that are moving rapidly, is a matter of common experience. Every housewife knows that dust blows in the doors and windows, but settles out on the furniture of the room. The cause of this lies in the fact that the dust particles cannot remain suspended in the air as soon as the velocity of the latter is sufficiently reduced. Advantage has been taken of this property of suspended particles to recover valuable material from the fumes at the Cananea,† Copper Queen,‡ and Anaconda§ copper works. The gases are conducted through chambers and galleries where the velocity is reduced to the necessary rate¶ before they pass out through the large stack.

* Hofman, Metallurgy of Copper, page 218; Hofman, General Metallurgy, page 831.

† Shelby, Eng. Min. J., **85**, 204 (1908).

‡ Lee, Eng. Min. J., **90**, 504 (1910).

§ McDougal, Canad. Min. Rev., **24**, 26 (1905).
Austin, Tr. A.I.M.E., **37**, 478 (1906).

¶ Kiddie, Tr. A.I.M.E., **40**, 900 (1909).

The researches of Kiddie,* Lee † and others have shown that the temperature must be below 300° C. and the velocity reduced to about 200 ft. per minute before the very small particles will fall out. In the downcomers and in some other parts of the plant the velocity may be as high as 1500 ft. per minute, hence it is obvious that enormous spaces must be erected for settling chambers. Fig. 34 is a diagram of the flues at Washoe smeltry, Anaconda, where some of the fumes travel four-fifths of a mile before they are allowed to pass into the final stack. Fig. 35 is a transverse section of the twin settling chamber. Over 80 tons of fume are collected every 24 hours by this plant. Particles that pass into the open from the plant are sufficiently fine to go through a sieve of 200 mesh. (Figs. 34 and 35.)

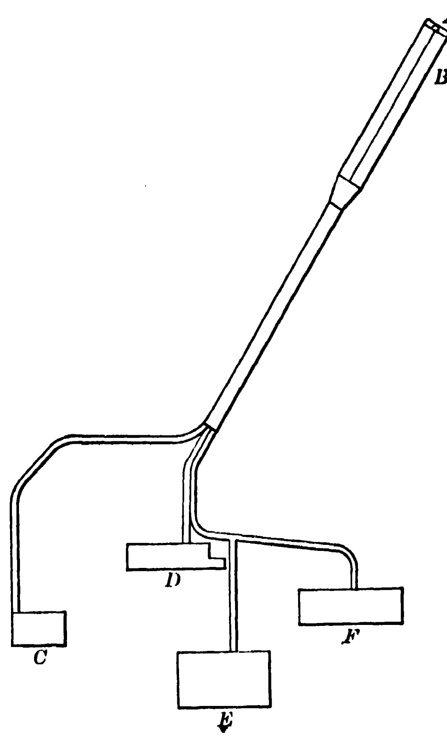


FIG. 34. Plan of flues at Washoe smeltry, Anaconda.

A is the stack, *B* the twin settling chamber, *C* the blast furnace plant, *D* the roaster plant, *E* the converter plant, and *F* the reverberatory plant.

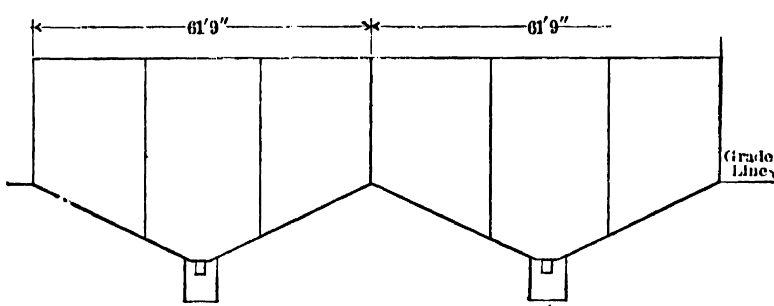


FIG. 35. Transverse section of the twin settling chamber at the Washoe smeltry, Anaconda. *A, A* are the tunnels where the precipitated fume is loaded into cars.

Arresting by Means of Baffle Plates or Wires. — The efficiency of the settling chamber is greatly increased by the installation of baffle

* *l. c.* † *l. c.*

plates or wires to arrest the progress of the dust. When the particles are brought into contact with one another on some surface, they form clumps that are not easily disintegrated. These clumps can therefore be shaken off the baffles by hand or by machinery without causing the particles to enter the air current again.

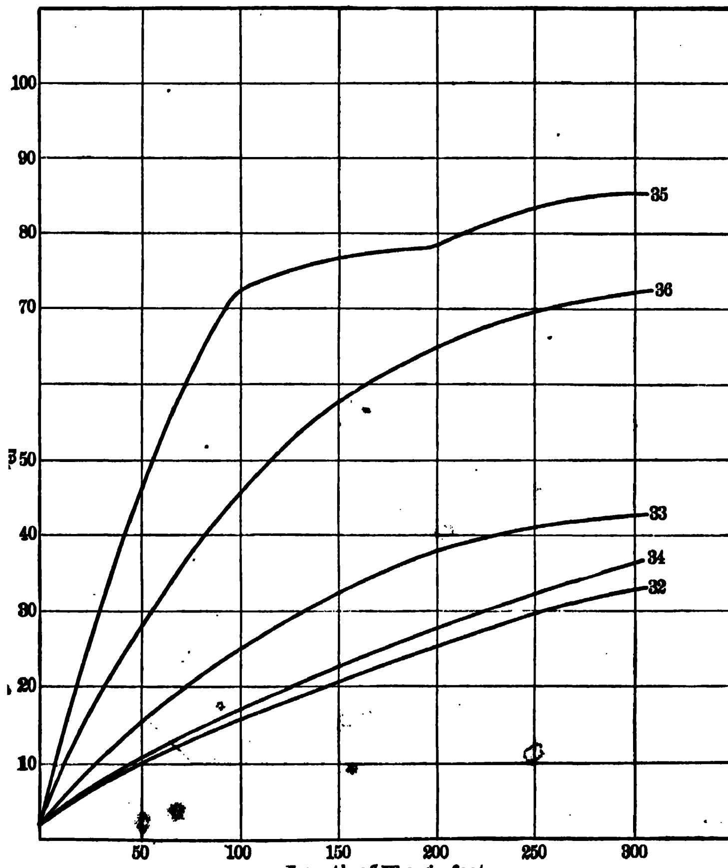


Fig. 36.

The Roesing wire system* is in successful operation at Great Falls.† Before the present system was adopted, elaborate experiments under actual working conditions were carried out with the various arresting devices. The results are shown graphically in Fig. 36. Curves 32 and 34 show that only 30 to 40 per cent of the dust was collected when the gases passed through the open or ordinary flue. Freudenburg plates,

* Hofman, General Metallurgy, p. 846 (1913).

† Herrick, Mines and Minerals, 30, 257 (1909).
Goodale, Tr. A.I.M.E., 40, 891 (1909).

suspended in such a manner that the gas current strikes the narrow edge,* increase the efficiency somewhat as shown by curve 33. When baffles, 3½ in. wide, are hung so that the gas strikes the side of the plates, the efficiency is 70 per cent, as shown by curve 36. Wider plates, 6½ in., curve 35, arrest still more of the dust; but the cross-sectional area is reduced 50 per cent, and as a consequence the draft is very greatly interfered with. Wire baffles give a high efficiency, and do not seriously obstruct the draft. There are about 1,200,000 steel wires in the system, placed 2.3 in. apart from center to center, and divided into two sets. One set is made up of No. 8W. and M. wires, each 16 ft. long, while the other is composed of No. 10 wire, 20 ft. long.

Filtering. — Filtering by means of woolen or cotton bags is another device employed to condense fume in the Mammoth Smeltery, Kennett, Cal.† Air is admitted to cool the gases to 100 degrees or less, and finely divided zinc oxide, or calcium hydroxide, is blown in to neutralize the SO_3. The neutralization is necessary or the bags would be destroyed within a few hours. The bag house is 210 ft. long, 63 ft. wide, and contains 3000 woolen or cotton bags, each 34 ft. long and 18 in. in diameter. About 10 tons of fume are collected every twenty-four hours by this means.

Electrical Precipitation, Cottrell Process. — The removal of suspended particles from gases by aid of electric discharge was suggested by Hohlfeld ‡ as a means of preventing the smoke nuisance, as early as 1824. While many attempts have since been made to render the method commercially useful, the efforts of Cottrell were the first to be crowned with success. The development of the process is interestingly told by the inventor in some of his publications.§ The principles involved are more or less familiar to every physicist, and consist in bringing the particles in contact with fine points having a high electrical potential. The particles thus become charged with the same sign as the fine points, and are attracted to and discharged upon a large plate electrode having the opposite sign, and a low potential. The precipitated material may be easily washed or shaken off the

* Hofman, General Metallurgy, p. 845 (1913).

† Campbell, Min. Sc. Press, **96**, 30 (1908).
Martin, Min. Eng. World, **29**, 309 (1908).
Rice, Eng. Min. J., **90**, 614 (1911).
Martin, Mines and Minerals, **33**, 323 (1913).

‡ Kastner Archiv. Naturl., **2**, 205–6 (1824).

§ U. S. Pats. 866843, 895729, 945917, 1016476, 1035422, 1067974.
Jour. Ind. Eng. Chem., **3**, 542 (1911).
Smithsonian Report, p. 653 (1913).
Mining Industry, vol. XXIII, p. 889 (1914).

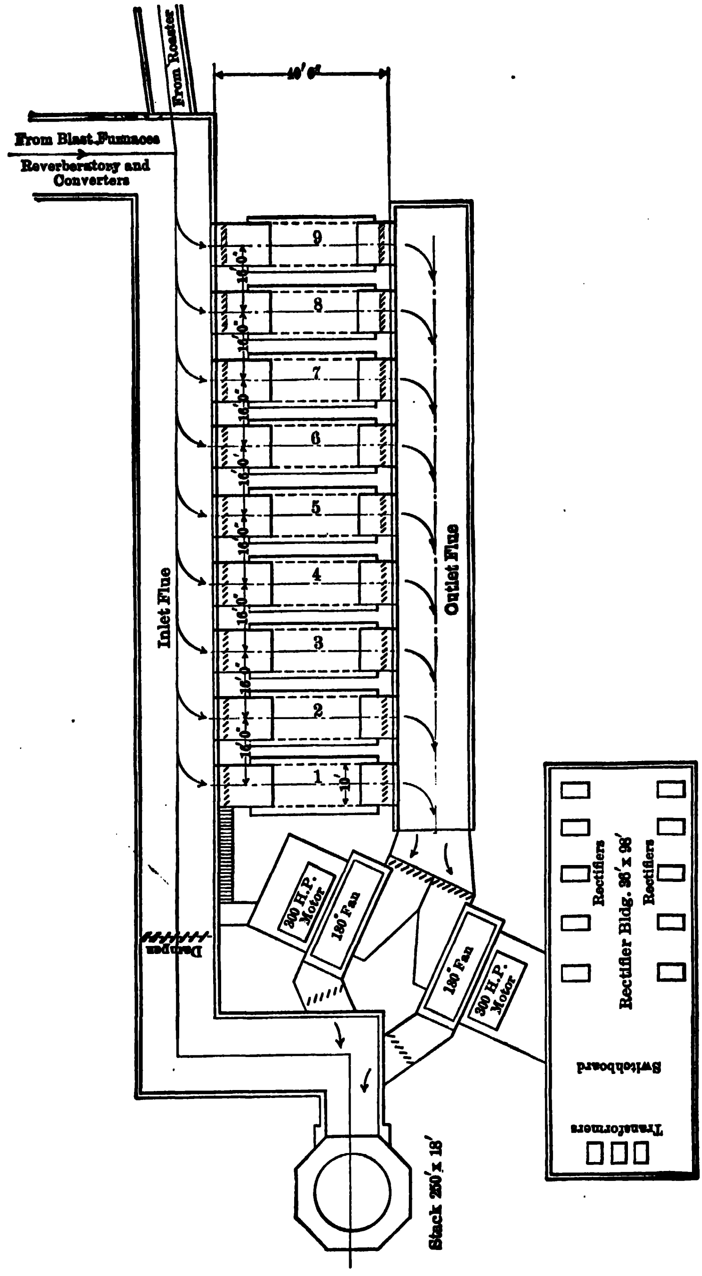


FIG. 37. General arrangement of precipitation plant, Balaklala Con. Copper Co., Coram, Cal.

plate electrodes, which in practice are usually lead or iron. The high potential electrodes are made of mica or asbestos and the fibers of the material serve as the necessary fine points. Direct current must be

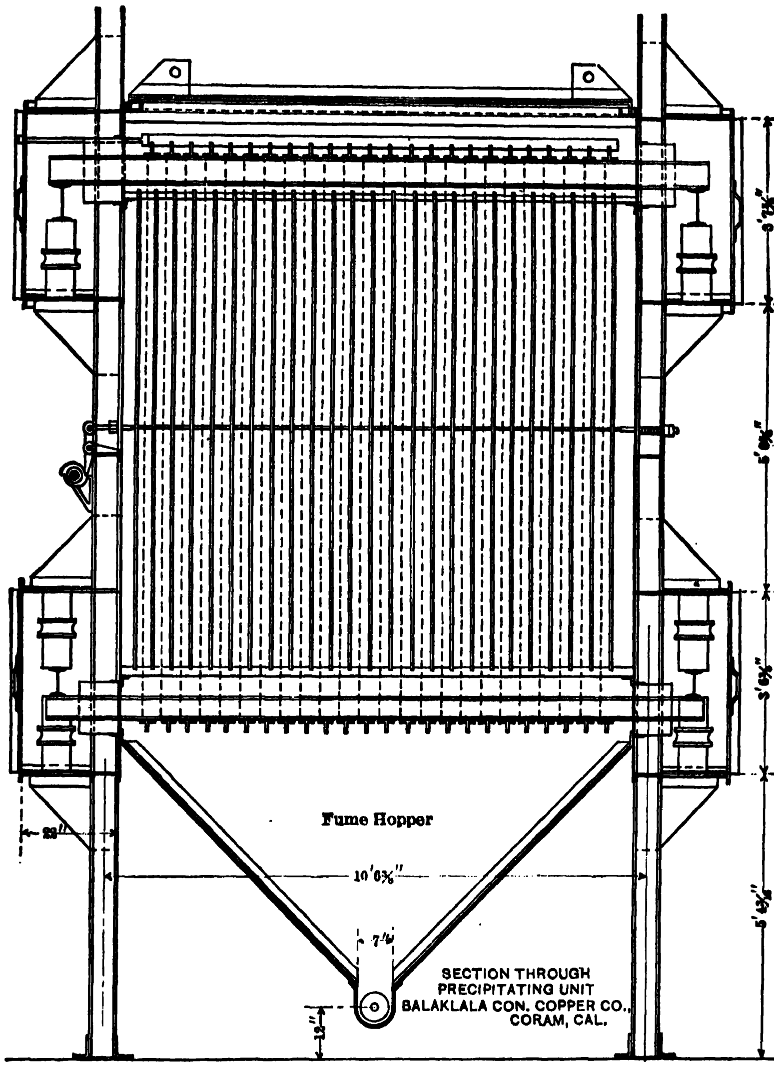


FIG. 38.

employed, and is obtained from an alternating current by means of rectifiers. The potential of the asbestos or mica electrodes is in some plants raised as high as 100,000 volts. The electrical method of precipitation is particularly adapted for use in plants where sulfuric acid

particles are present in the fume. The acid recovered often pays the cost of operation several times over.

The electrical method was installed in the Balaklala Copper Works, Coram, Cal., after many tests had been made with other methods of precipitation. Fig. 37* is a plan of the nine electrical precipitation units, or chambers, in their relation to the flue system and stack. The large fans are not necessary for the operation of the precipitation system, but are employed to dilute the flue gases with air in order to reduce the concentration of the sulfur dioxide below the maximum allowed by law, *viz.*, three-fourths of one per cent. Fig. 38 shows a cross section through one of these units. The double lines represent the collecting electrodes, each 6 inches wide and 10 ft. long, made of No. 10 sheet iron. The dotted lines are the high potential electrodes. 200,000 to 300,000 cubic of gas at a temperature of 100 to 150° C. pass through this system per minute under normal working conditions, and 6 to 8 tons of precipitated material are collected every 24 hours.

The electrical process has been installed by the Riverside Portland Cement Co. near Riverside, Cal., where nearly 100 tons of dust are collected every 24 hours. The dust contains considerable K_2O which is worked up into valuable fertilizer. The process is employed in many silver, zinc, and arsenic plants, and is working successfully at Catasauqua, Pa., for the recovery of volatilized potash from feldspar. At the North Works of the American Steel and Wire Company, Worcester, Mass., it is employed for collecting volatilized hydrochloric acid. An electrical process based on the same principles is controlled for the State of California by the Petroleum Rectifying Company,† San Francisco, for the dehydration of crude petroleum. The oil and water form an emulsion sometimes very difficult to separate into two layers.

* Figs. 37 and 38 are taken from an article by F. G. Cottrell in the Jour. Indus. and Engineering Chem., 1 (1911).

† Oil Age, April 21 (1911).

CHAPTER XV

RUBBER

The study of the physical and chemical properties of rubber has received a decided impetus as a result of recent developments in colloidal chemistry, for it cannot be denied that in caoutchouc, the fundamental substance from which commercial rubber is made, we have a typical colloidal body. Many of the processes in the manufacture of both the crude rubber, caoutchouc, and the finished product, rubber, such as the coagulation of the latex, find no explanation from the purely crystalloidal chemical standpoint. Unfortunately in the discussions on the subject it has not always been recognized that in most instances both the colloidal and crystalloidal processes take place simultaneously. Consequently important facts are often ignored by the extreme advocates of the colloidal and the purely chemical schools. Only by a proper perspective involving both views, can we arrive at the true explanation of many of the phenomena connected with the chemistry of rubber.

The Latex

The latex from which caoutchouc is obtained is a milk-like fluid differing somewhat in its properties according to its origin. Biologically it is the sap of certain trees or shrubs; chemically it is a disperse system consisting of globules of caoutchouc suspended in a watery liquid.

A chemical analysis of the latex from Funtumia elastica gave the following results:

	Per cent
Water (reacts acid)	56.9
Caoutchouc	36.53
Resins	4.16
Protein and minerals	2.88

The simplest formula that we can give to caoutchouc is Un, where $U = C_5H_8$. Many chemists believe that U should be given the value $C_{10}H_{16}$. In either case caoutchouc may be considered as a condensation product of isoprene, C_5H_8.

As might be expected from the standpoint of colloidal chemistry, molecular weight determinations of caoutchouc in solvents give unsatisfactory results. This is accounted for by the fact that the average n is large, and the osmotic pressure correspondingly low. Therefore the lowering of the freezing point becomes negligible.

Wo. Ostwald, E. Fickendey, V. Henri and others have classified the latex as an emulsion, class 5, page 28. On the other hand it is strenuously contended by Ditmar * that the globules are solid particles, and the latex must therefore be considered a coarse suspension, class 4. C. O. Weber † considers the globules are composed of liquid terpenes surrounded by a protective layer of protein (Hevea braziliensis), or peptone (Funtumia). Other authors, notably J. Henri ‡ and E. Fickendey, § accept the idea of a protective layer, but believe that the substance of the globules is caoutchouc. The last named author regards the caoutchouc in the globules as a liquid, claiming that it becomes a solid only on coagulation. Whether the latex is to be regarded as a suspension or an emulsion is not of paramount interest to the industrial chemist, however.

Charge and Brownian Movement. — The particles or globules in the latex are charged negatively and are in rapid motion. This phenomenon is termed "Brownian Movement." See page 40.

Source. — The trees, shrubs or vines that yield the latex are found in warm climates under the most varying conditions of soil and moisture, and belong to the botanical orders, Euphorbiaceæ, Apocynaceæ, Urticaceæ, Compositæ. Para rubber comes from Hevea braziliensis, formerly called Siphonia braziliensis, which grows wild in Brazil in hot moist climates, and is now cultivated on rubber plantations in Asia, notably Ceylon, and in the Malaya Peninsula. Ceara or Manicola rubber is obtained from Manihot Glaziovii, a tree that grows on dry rocky soil in South America. "Caucho" rubber comes from Castilloa elastica which grows in Peru. The same tree in Central America yields "Ule" rubber. Guayule rubber is obtained from the Guayule shrub which grows in Mexico under almost desert conditions. In Africa the chief sources of native rubber are Funtumia elastica, or Kickxia, and the Landolphia vines. In Asia rubber is obtained from a wild tree, Ficus elastica, in addition to the many cultivated varieties of rubber producing plants.

Size of the Particles. — The suspended globules of caoutchouc found in the latex vary in size within comparatively wide limits. Those of Hevea have been found by Fickendey to have a diameter of 0.5–2.5μ. On the other hand, few particles in the latex of Funtumia have a diameter as great as O.Iμ, and the milk appears almost homogeneous under the most powerful microscope.

* Der Kautschuk, p. 23 (1912).
† Gummi Zeit., No. 7 (1902).
Ber. d. Deutsch. chem. Ges., 3108 (1903).
‡ Le Caoutchouc et la Guttapercha, No. 27 (1906).
§ Kobloidzeitschr., **8,** 43–7 (1911).

Coagulation of the Caoutchouc.

The methods in practice for the separation of the caoutchouc from the watery liquid are:—

1. Heat and smoking: employed by the natives for preparing Para rubber.
2. Boiling: Funtumia.
3. Evaporation: drying on the bark as it runs down the wound, whereby elastic strings called "scrap" are obtained; or, pouring the milk into saucer-shaped stumps where the water is either soaked up by the wood or evaporated into the air. The masses of rubber so obtained are called "cakes."
4. Dilution with water.
5. Addition of precipitating agents: acids, alum, etc., are usually employed on rubber plantations.

One and the same method of coagulation is not always applicable to the latex from different sources, consequently in practice that method must be sought out which will produce the best caoutchouc from a given latex. The problem of choosing the most efficacious method is further complicated, however, by the presence in the latex of either protein or peptone, both of which act as protective colloids for the globules. Moreover it is stated by some experimenters that the composition of the latex varies with the season of year and even with the height from the ground of the incision in the bark. On the other hand J. v. Wiesner has found that the resin in the latex of the euphorbiaceæ is independent of the geographical distribution.

The objections to be raised against the first and third methods, *viz*, heating and smoking, and evaporation, are that many of the undesirable constituents such as dirt, bark, resin, protective colloids, etc., are left in the coagulant, caoutchouc. Some of these substances can be removed, of course, by subsequent treatment such as grinding and washing, drying in air or vacuo, but mineral matter, resins, and proteins still remain and cannot be eliminated except by expensive processes. It must be confessed, however, that Para rubber obtained by the natives of Brazil is superior to that made by the most scientific methods yet devised on plantations. It is a matter not yet decided whether the superiority of Para rubber is due to the method, or to the inherent qualities of the latex.

According to the researches of E. Fickendey all varieties of latex may be coagulated by boiling. This operation destroys the protective colloids and the coagulation is then caused, or at least aided, by the electrolytes present in the natural milk.

To V. Henri, and later to E. Fickendey, we are especially indebted for a clear presentation of the process of coagulation and of the effect of precipitating agents. According to these investigators the process takes place in steps, and may be followed to some extent under the microscope. During the first step, depending upon the method employed, the globules may gather together and form clumps, where the particles touch one another but do not flow into a compact, elastic mass; or long filaments may be formed. The clumps, or flocks, may remain suspended in the liquid or may sink to the bottom and finally form a powder. Mechanical agitation will merely subdivide the flocks, and the process therefore resembles the coagulation of blood. Henri calls this phenomenon agglutination. In case long fibers are formed a further action takes place during which the particles flow together and form an elastic net work. The formation of an elastic mass from the net work is accelerated by boiling, or by mechanical manipulation.

There is a want of conformity of opinion among different investigators with regard to what actually happens during the last step. If the particles are composed of liquid caoutchouc surrounded by a film of protective colloid, then we must conclude that a solidification occurs as well as coagulation. Some writers are inclined to the belief that a polymerization takes place whereby larger molecules are formed. According to E. Fickendey this is a pure but not impossible assumption for which we have no direct experimental proof.

Effect of Precipitating Agents.—In practice we are interested in the effect of precipitating agents on the latex as it comes from the tree, but in order to find the scientific basis for this effect it is necessary to eliminate all the dissolved salts already present in the natural milk. This was effected by Henri on the latex from Hevea braziliensis by means of dialysis through collodion filters, see page 36. His results may be summarized as follows:

1. Alcohols were without effect. Up to this time alcohols had been considered universal precipitants for caoutchouc, but we can now safely conclude that the precipitation is due to the combined effect of alcohol plus the dissolved electrolytes.

2. Salts of the alkaline metals likewise cause no precipitation.

3. Salts of the alkaline earth cause formation of flocks.

4. Salts of the heavy metals at a much smaller concentration cause formation of flocks. In none of these cases however is an elastic mass formed.

5. Alkalis have little effect.

6. Acids cause the formation of flocks. HCl, HNO_3, Hac, have approximately the same effect. H_2SO_4 is much more efficacious and

very dilute trichloracetic acid causes the separation of an elastic mass.

8. Alcohol + salts of univalent metals at high concentration cause flock formation.

9. Alcohol + acids, or salts of bivalent or trivalent metals, give an elastic mass.

10. Alcohol + alkalis do not cause coagulation, but on the contrary retard the action of other precipitants.

It will be noticed that the behavior on the part of precipitating agents is analogous to the effect on protein (see page 216). While the evidence is not conclusive, it is nevertheless probable from our knowledge of protective colloids, that the protein film on the outside of the globules must be destroyed before an elastic mass can be formed. Any solvent or precipitant for protein should, therefore, leave the globules more or less free to unite after their electric charges have been neutralized by an electrolyte. The salts of the heavy metals coagulate protein. This accounts for their precipitating action on the latex. This point of view is further strengthened by a research on Kickxia latex by E. Fickendey.* It was known that this latex would not respond to the usual precipitants. The cause of this peculiar behavior was found to lie in the fact that Kickxia latex contained peptones but no proteins. Precipitating agents for proteins would, therefore, have no effect, while those for peptones, such as tannin, would cause coagulation.

D. Spence † has investigated the effect of precipitating agents on the latex, Funtumia elastica, in the natural state. His results are in keeping with those of Henri except, of course, that the latter worked with the dialyzed latex.

Crossley has found that the acid used for coagulation is adsorbed according to the laws that usually obtain for colloids (see page 52). Hence some of the acid should be adsorbed on the globules and carried down in the elastic mass from which it could be removed only with great difficulty. This is in agreement with facts.

According to the ideas laid down in the introduction to Part II, the coagulation of the latex may be explained as follows: Precipitating agents that do not dissolve or coagulate the protective colloid may cause the flock formation because the electric charges are neutralized and the particles join by surface contact only. Thus no increase of n is involved. On the contrary precipitating mixtures that destroy the effect of the protective colloid and neutralize the electric charges at the same time allow the particles to flow together, whereby n is

* E. Fickendey, *l. c.*

† Liverpool University. Institute of Commercial Research in the Tropics.

greatly increased and an elastic mass or net work results. It is also possible that during the formation of the solid from the liquid caoutchouc some change of U takes place, but this is not necessarily true.

Vulcanization

When raw caoutchouc is mixed with sulfur and the temperature raised sufficiently a remarkable change of chemical and physical properties takes place. The mass loses its adhesiveness, called "tackiness" in practice; the elasticity may vary between great extremes; differences of temperature over a comparatively wide range have little effect; it is rendered insoluble in any liquid that does not permanently destroy it; and finally it is much more resistant to oxidation, and therefore less liable to "perish." The process is known as the "hot cure" or hot vulcanization. Similar alterations in properties, differing only in degree, may be brought about by what is termed the "cold cure," or cold vulcanization. The hot cure is much more widely applied in practice.

Cold Vulcanization. — The material in thin strips, or sheets, is passed through, or dipped into a solution of sulfur chloride (S_2Cl_2) in carbon disulfide, or carbon tetrachloride. Some of the sulfur chloride remains united, physically or chemically, with the caoutchouc, and the excess is neutralized with ammonia. By this process the goods acquire a soft velvet feel, but unfortunately are liable to "perish" rather easily. A variation of the method, technically known as the vapor "cure," consists of treating the goods with the vapors of sulfur chloride. Subsequent neutralization with ammonia is, of course, necessary.

Hot Vulcanization. — This process is carried out in one of three ways:

1. By steam heat where the sheets are wound on a drum, covered with a steam-proof wrapper, and subjected to a steam pressure of several atmospheres.

2. Where massive articles are to be vulcanized a hot press, or mould, is found most convenient. This is termed the "press cure" and is the usual method employed in the manufacture and repairing of pneumatic tires. In both these methods accelerators are often added together with a varying amount of "fillers." Litharge is frequently used as an accelerator for black goods, and lime or magnesia for white. Litharge cannot be employed for white goods because of the lead sulfide formed during the heating.

3. Boots, shoes, coats, etc., are usually vulcanized by the "dry heat cure." Here the goods are hung in an air-tight chamber heated by steam. Litharge or other accelerators are necessary to accomplish the purpose in a reasonable length of time — six to seven hours.

In order to produce a soft rubber the amount of sulfur added may

vary from 2 to 10 per cent. Of this amount usually not more than 3 per cent becomes so fixed that it cannot be extracted by the use of such solvents as acetone. This fixed sulfur is generally termed "combined." Under ordinary conditions in practice, regardless of the amount added, all the sulfur does not become "combined," but a portion, varying with the temperature and the duration of the heat treatment, always remains "free," *i.e.*, can be removed by solvents. For the production of hard rubber, or vulcanite, as much as 30 to 35 per cent of sulfur may be added, but it seems to be the general consensus of opinion among chemists that not more than 32 per cent ever becomes combined. If the amount of free sulfur is too great, a portion of it crystallizes out on the surface in the form of a pale yellow deposit. This phenomenon is known as "blooming." In order to prevent the crystallization of the sulfur on the outside of certain goods the amount of free sulfur must be kept low.

The amount of sulfur necessary to give certain properties, such as a desired elasticity, depends a great deal upon the physical state of the caoutchouc. In general if the average value of n is lowered, by mastication, for example, more sulfur will be necessary to produce a desired result.

No substance has as yet been found that can adequately replace sulfur in the hot cure. Selenium does this only to a very limited extent and the result is not at all satisfactory. In the case of the cold cure some success has been obtained by the use of bromine in carbon disulfide.* Hypochlorites and hypochlorous acid have also been used.

Theories of Vulcanization

A great deal of work has been done of recent years on the process of vulcanization. Unfortunately the results of one experimenter often seem to contradict those of another; consequently we have few undisputed facts upon which to base our theories. This want of accord among the experimental results is probably not due so much to inaccurate work as it is to the fact that raw caoutchouc is a complex product, varying in properties to a considerable degree with its source, method of preparation, age, etc. A short summary and not an extended discussion of the two principal theories will be given here. For a more comprehensive review of the subject the reader is referred to the original literature, or to "Der Kautschuk" by Ditmar.

The Chemical Theory. — The first to suggest this theory as an explanation of his own experimental results was C. O. Weber.† His conclusions may be briefly stated as follows:

* C. O. Weber, Chemistry of India Rubber (1906).

† Zeit. f. angew. Chemie, **112**, 142 (1894).

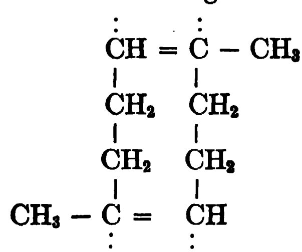
1. Caoutchouc unites with sulfur without the evolution of an appreciable amount of hydrogen sulfide. The reaction is therefore an addition process.

2. A continuous series of compounds is formed, the highest member of which probably has the formula $(C_{10}H_{16})_{10}S_{20}$, while the lowest may be represented by $(C_{10}H_{16})_{10}S$. Which member of the series is formed depends upon the amount of sulfur added, the temperature and the duration of the treatment.

3. The physical state of the raw material does not determine the end-point, but may affect the time and temperature factors.

4. During cold vulcanization with S_2Cl_2 a similar series is formed. The highest member of this series would therefore have the formula $(C_{10}H_{16})_{10}(S_2Cl_2)_{10}$, and the lowest $(C_{10}H_{16})_{10}S_2Cl_2$.

The above theory has been extended by Ditmar to include the work of Harries and Hübener.* According to this explanation the molecule of caoutchouc has the following formula.



Ten of these groups or molecules are loosely united by the dotted lines into a huge ring-formed entity. Sulfur or sulfur chloride may be added to the caoutchouc at any one or more pairs of double bonds.

Expressed in the scheme of the introduction $U = C_{10}H_{16}$ in which there are two double bonds, and $n = 10$. During the process of vulcanization alterations in adhesiveness, elasticity, resistance to chemical reagents, solvents, etc., are therefore due essentially to a chemical change in U, owing to the addition of sulfur or sulfur chloride.

The Adsorption Theory. — Wo. Ostwald † has suggested that the addition of sulfur is a purely additive process similar to other adsorption phenomena where we are certain that there is no chemical combination. He offers the following arguments in favor of this theory:

1. The addition of sulfur may be represented by the adsorption equation

$$\frac{x}{a} = k \cdot c^m$$

* Chem.-Ztg. Jahrg., **33**, No. 17, 144–5 (1909); No. 18, 155–7 (1909); No. 71, 648–9 (1909); No. 72, 662–3 (1909).

† Kolloidzeit, **6**, 136–155 (1910); **10**, 146–148 (1912); **11**, 38–39 (1912).

where x is the amount adsorbed, a the amount of the adsorbing substance, c the initial concentration of the substance adsorbed, and k and m are constants. The equation also holds for the addition of sulfur chloride.

2. The existence of a continuous series of addition compounds in the same mass, and formed at the same time, is improbable, and is unknown elsewhere in chemistry.

3. None of the intermediate members of the series have ever been isolated from each other.

4. The apparent constant relation between sulfur or sulfur chloride and caoutchouc obtained by several authors working with a large excess of the substance to be adsorbed, can be explained by the fact that they were on the portion of the curve, Fig. 39, where it runs asymptotically to the abscissæ. In other words they had arrived at a

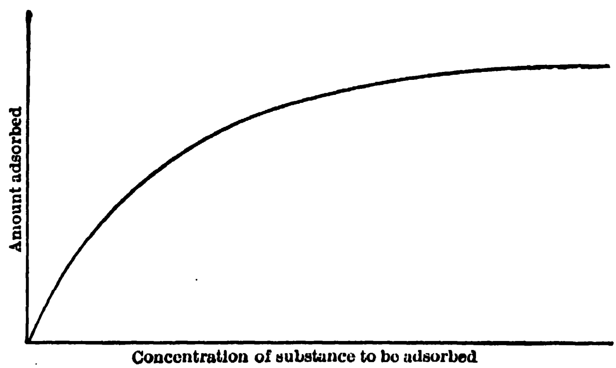


FIG. 39. Concentration of substance to be adsorbed.

state of maximum adsorption from the standpoint of analytical chemistry, because further increases in the adsorbed sulfur are too small to be detected.

C. O. Weber and later D. Spence and J. Young * claim to have found 32 per cent to be the maximum amount of sulfur that can become fixed. This would correspond to the formula $C_{10}H_{16}S_2$. Moreover Hinrichsen and Kindscher obtained a body by cold vulcanization that from analysis should have the formula $(C_{10}H_{16})_2S_2Cl_2$. From this body they formed another substance by the breaking off of hydrochloric acid. The results of the analysis would suggest the formula $(C_{10}H_{15})_2S_2$.

5. The temperature coefficient as determined from the results of C. O. Weber is 1.8 and hence too low to be that of a chemical reaction. The latter vary from 2 to 3 according to van't Hoff's rule. D. Spence and J. Young have since found 2.65 to be an experimental value.

* Kolloidzeit, **11**, 28–34 (1912).

6. The amount of sulfur that becomes "fixed" during vulcanization depends not only upon the temperature and the duration of the treatment, but also upon the previous history of the caoutchouc. This cannot be explained on any chemical theory. On the contrary we should expect this peculiar behavior if the sulfur is being adsorbed by the caoutchouc, because the molecular aggregates of the latter will vary with the method of preparation.

7. Hinrichsen and Kindscher* have shown that all the sulfur may be extracted from cold vulcanised rubber, and they claim to have reduced the so-called combined sulfur in hot vulcanized rubber to a very large extent. The extraction follows a typical adsorption curve, and the process of vulcanisation is therefore a reversible one, although this point is not necessary for the adsorption theory.

Objections to the adsorption theory have been raised by several authors. W. Hinrichsen has pointed out that adsorption phenomena are equilibria and can for that reason be reached from both sides. No one has ever succeeded in completely extracting all the sulfur from hot vulcanized rubber, consequently it is improbable that the process is reversible. It may be said with regard to this statement that it is cumulative evidence but not a convincing argument, because a portion of the sulfur may be enclosed by the rubber with the result that all of it could not be extracted without destroying the substance. Another argument of Hinrichsen's seems well grounded, — to wit, adsorption equilibria are quickly and easily reached, while the reaction between sulfur and caoutchouc continues for many hours even at higher temperatures. In fact it has been shown by Spence that all the sulfur, up to 10 per cent at least, would unite if the process is kept up for a sufficiently long time.

Hinrichsen further remarks that other derivatives of caoutchouc such as *the tetrabromide* are known. Vulcanized rubber can be changed quantitatively into this bromine derivative where the sulfur is almost exactly equivalent to the bromine. Furthermore the changes in properties during vulcanization are too fundamental to be explained on the basis of the adsorption theory. He concludes from the evidence that some of the sulfur, doubtless the free sulfur, is adsorbed, while the remainder is combined chemically.

D. Spence and J. R. Scott† have concluded from their results that sulfur is present in rubber in three different states, free, adsorbed, and chemically combined.

It may be said in defence of the chemical theory that it is entirely

* Kolloidzeit, **6**, 202–209 (1910); **10**, 146–148 (1912); **11**, 38–39 (1912).

† Kolloidzeit, **8**, 304–312 (1911)

unnecessary to assume the existence of a continuous series of addition compounds between caoutchouc and sulfur or sulfur chloride. Moreover it is also improbable that n has any fixed value except where a definite chemical compound is formed.

Regeneration of Rubber

The problems involved in the regeneration of rubber are exactly opposite in character to those of vulcanization. During the latter process the endeavor is made to render the mass less plastic, less soluble in reagents, and more inert chemically. During regeneration on the other hand the end in view is to re-establish the original properties of the caoutchouc. As sulfur during the vulcanization process has been the cause of the pronounced alteration of properties, it is obvious that regeneration will consist to a large extent in the extraction of the sulfur. We have seen, however, that all the sulfur cannot be removed completely. This fact explains to a large degree the inferiority of reclaimed rubber as compared to the original substance.

E. J. Fischer * has compiled a list of the various patents issued in Germany, France, England, and the United States during the last 25 years, for the recovery and regeneration of rubber. A study of these patents reveals the fact that the various methods are based on three salient factors, a rise in temperature (sometimes under pressure), solution, and mechanical manipulation.

With regard to the first of these we know that the plasticity of colloidal substances may be increased by a rise of temperature. This is probably due to a decrease in viscosity accompanied by a lowering of the value of n. Doubtless both of these factors operate in the case of rubber. In practice the high temperature and pressure are often obtained by the use of steam.

Solution also tends to decrease the value of n. Any solvent that attacks the sulfur, the vulcanized rubber, or the "filling" will tend to increase the plasticity. The solvents employed are acids, alkalis, naphtha, benzine, pyridine, and many others.

Mechanical manipulation tends to lower the value of n and therefore increase the plasticity. The process may be carried out during the action of the heat and solvents, or it may be a subsequent treatment.

* Gummi-Industrie, 4, Nos. 1, 2, and 3.

CHAPTER XVI

TANNING

The raw substance of which leather is made and the finished product are both colloidal in nature. The hide substance is a condensation product, or products, of several amino acids. The cell walls and the cell contents are very similar in chemical composition, but the latter are much more soluble. The cell walls are, however, capable of dehydration, and also of rehydration to form a gel. The cell substance is doubtless composed of larger aggregates than the cell contents. In either case the unit is complicated and may be represented by Un, where $U = U'n' + U''n'' \ldots$ etc. In the cell substance n would therefore have a larger value than it would in the cell contents.

The process of tanning consists essentially of three steps: First the rehydration of the partially dried hide; second the removal of the hair by the action of alkalis or alkali sulfides; third the precipitation of the hide substance by the action of tanning reagents, such as tannin, or the hydroxides of metals.

Rehydration and Swelling. — While water alone will soften the hide substance, causing it to swell, the reaction is much more rapid in dilute acid or alkali solution. For the production of soft thin leather the hides are soaked in a dilute alkali solution. The action of acids ("pickling"), such as dilute sulfuric acid, is more intense, and is resorted to where thick hides are used to produce sole leather or heavy belting. The swelling is entirely analogous to that of gelatin,* and has been explained by some chemists in the following manner. The cell substance, possessing both free amino and carboxyl groups, is an amphoteric electrolyte, and can therefore function as an acid or as a base. Although the basic property is somewhat the stronger, the dissociation is very small and the osmotic pressure correspondingly low. When the hide comes in contact with the solution of acid or alkali a highly dissociated salt is formed with the amphoteric contents of the cell. The osmotic pressure is greatly increased as a consequence and water entering the cell causes distention or swelling.

The swelling process must not be continued too long else the cell walls begin to disintegrate into a more soluble and mechanically weaker substance. The disintegration is greatly aided by the presence of cer-

* Koll. Chem. Beihefte, 2, 243–284 (1911).

tain ferments and especially by the hydrogen ion, hence there is danger involved in pickling with acids.

The tanning proper is carried out by the use of tannin, or vegetable extracts, or by minerals such as the salts of iron, aluminium, and chromium. The function of the tanning agent is to form an insoluble precipitate with the components of the hide. This takes place usually in acid solution. The resulting insoluble substance, leather, is much more inert chemically than the hide, and as it is insoluble in water there is no increase of osmotic pressure and hence no appreciable swelling.

Whether the combination of the tanning agent with the hide substance is purely chemical, or whether the reaction is to be explained as an adsorption of one substance by another, or the coprecipitation of two colloidal substances having electric charges with opposite signs, is still a controversial matter.* The vegetable extracts used for tanning purposes are all colloidal in solution. In mineral tanning a colloidal gel, for example, iron, aluminium or chromium hydroxides, is formed in the fibers. The reduction of bichromate in the fibers is aided by reducing agents.

Adsorption undoubtedly plays an important part in the first stages of the tanning proper. At first considerable quantities of the tanning agent may be washed out, while the hide has not fully acquired the properties of leather. As the hide becomes more and more leather-like the amount of the tanning agent that can be extracted by water decreases. This may mean that secondary chemical changes are taking place, or that the insoluble substance formed on the outside of the aggregates is somewhat impermeable to the reagent, and that considerable time is necessary for the penetration of the tanning agent into the center of the aggregate.

In practice gradual tanning is aimed at. This is accomplished by treating the fresh hide with the spent liquor, so that the least adsorbable constituents will be adsorbed first. The partially tanned hide is then treated successively with liquors containing more easily adsorbable constituents.

Chromium salts are more advantageous for tanning than either those of iron or of aluminium, although aluminium salts are perceptibly better than those of iron. The reason given is that the latter are hydrolized too greatly, and the salt, therefore, does not so easily penetrate the cell substance. The effect of iron salts can be improved by the aid of protective colloids such as blood, albumin, gelatin.

* See Chapter XI on dyestuffs.

CHAPTER XVII

MILK

Milk is a complicated colloidal system * containing three distinct disperse phases: fat, casein, and albumin. The colloidal properties of albumin and casein have been adequately dealt with in Chapter XII, so that for the present purposes it will be necessary to treat only the fat constituent of milk. The considerations taken up here are further restricted to cow's milk.

Size of Fat Particles. — The diameter of the fat particles differs between the extremes 0.1 μ and 22.2 μ. The size is dependent upon many factors such as the breed of cattle, food, stage of milking, health of cow, and length of time since freshened. The average size for Jersey cattle is 3.5 μ; for Shorthorn 2.92 μ. The average diameter is somewhat larger toward the end of the flow than at the beginning of the milking. The particles diminish in size after the cow has been milking some months.

Coagulation of Fat Particles. — The casein and the albumin act as protective colloids for the fat particles, hence it is necessary to offset this protective effect before the fat or butter can be obtained free from the casein. It is generally believed that the casein forms an envelope around the fat particles, but other explanations of protective action have been offered.†

The fat particles rise to the top if the milk is allowed to stand, carrying part of the casein with them. The cream may also be separated from the major portion of the liquid by centrifugal motion. This is, of course, the principle of the cream separator. The fat may be further freed from the casein by severe mechanical agitation, called churning in practice, but only with great difficulty can this be done if the cream has not become sour. The effect of the mechanical process is ascribed to the rupturing of the casein envelopes by the agitation. The fat being now unprotected rises to the top and "gathers" to form butter.

The fat may be separated quickly from the liquids if acid is added. Small amounts of sulfuric acid precipitate the casein, and the fat now being unprotected comes out with the casein. On the other hand if concentrated sulfuric acid is added the casein is dissolved, owing to its

* Wiegner, Kolloidzeit, **15**, 105 (1914).

† Theories of Protective Colloids, page 111.

amphoteric character, and the fat separates out free from other substances. Alkalis also dissolve the casein and hence allow the fat to coagulate. The fact that butter is more easily obtained from soured than from sweet cream can be explained on the ground that the lactic acid formed destroys the protective action of the casein by precipitating it.

Homogenization. — Fundamentally this is a process for mechanically increasing the degree of dispersion of the fat. This is accomplished by forcing the milk, which is heated to about 85 degrees, between iron plates. The pressure sometimes reaches 250 atmospheres. The particles of fat are reduced to about one-tenth their former size and exhibit a vigorous Brownian movement.

Not only can the fat particles already in the milk be reduced in size, but the cream that has been skimmed off can be redispersed. Moreover certain oils can be substituted for the natural butter fat. It is necessary, however, that casein be present in the liquid in which the fat is to be redispersed else the latter separates again. It is interesting to note that a very much larger portion of the casein is adsorbed by the homogenized fat than by the particles in their natural state. The system is also more stable for the cream no longer rises to the top, nor can the fat be separated by centrifugal motion. The increased adsorption and the greater stability are both in agreement with the usual behavior of other colloidal systems when the degree of dispersion is increased.

Homogenization is employed to a large extent in the manufacture of ice cream. When the natural cream is frozen comparatively large crystals of ice are formed, which give a rough feeling on the tongue. In homogenized cream the number of fat particles is about one thousand times greater and therefore the spaces between the particles are small. As a consequence when the homogenized cream is frozen the ice crystals are too small to be noticeable. The product is said to be "smoother." The white of eggs is often added to prevent the formation of large ice crystals.

CHAPTER XVIII

COLLOIDAL GRAPHITE

Although carbon is found in a very fine state of subdivision in many oils, coal tars, etc., the best known example of colloidal carbon is "Deflocculated Acheson's Graphite"* in water or oil suspension. These solutions are known technically as "Waterdag" and "Oildag" respectively, names given to them by the inventor, and are used extensively in lubrication.

The preparation of these solutions was rendered possible by two interesting observations made by Acheson in connection with the graphite crucible and the carborundum industries. He knew that the German clays used as binding material in the production of graphite crucibles possessed greater plasticity than American clays of similar composition. He had also observed that American clays taken some distance from their source were more plastic than those lying near the spot where they had been formed by the decomposition of the original rock. These two facts led him to conclude that the organic constituents had something to do with the plasticity of clays. His second observation bearing on this subject was that carbon in an extremely fine state of subdivision occurred in the furnaces employed in the manufacture of carborundum. He rightly concluded that this graphite was formed by the decomposition of carbon compounds in the intense heat of the furnace. It was found that on masticating graphite formed in this manner with gallotannic acid stable solutions of colloidal graphite, containing as much as 1 per cent of graphite, could be obtained thereby. In order to produce an oil suspension it was first necessary to make a paste of graphite and tannin in water. Oil could be gradually substituted for the water during the mastication and the oil paste diluted to the desired consistency.

The solutions thus formed behave in every way like other colloidal systems. The particles have a diameter of about 75 $\mu\mu$ and may be precipitated by the action of acids. It has not been possible from the literature to decide whether the tannin employed to deflocculate the graphite is a true peptising agent, or only a protective colloid.

* Journ. of the Franklin Instit., **164**, 375 (1907).

CHAPTER XIX

CLAYS AND SOILS

Clays are hydrated mixtures of silicates, *viz.*, iron, aluminium, the alkalis, and alkaline earths. Some sand, mica, feldspar, and organic matter are also usually present. The grains of the constituents are more or less surrounded by colloidal silica, silicates, hydroxides of iron, aluminium and manganese, and colloidal organic matter such as humus. The amount of inorganic colloidal matter is usually small, and varies, according to Schloesing,* from 0.5 to 1.5 per cent. If too little is present, the clay is called weak, lean, sandy, and has a low plasticity. On the other hand a large amount of inorganic colloids makes the clay fat, strong, and sometimes sticky instead of plastic. A plasticity suitable for modeling or ceramics, therefore, necessitates a proper relation between the proportions of colloidal and granular matter.

The effect of colloidal matter in clays is not confined to plasticity alone for the same constituent acts as a binder, and is responsible for the shrinkage and cracking during firing. Highly colloidal clays shrink more than others and crack badly on being dried. The incorporation of granular matter increases the strength of the ware by reducing the shrinkage and preventing to considerable extent the formation of these cracks. Frequently highly colloidal clays are preheated before mixing. The effect of this treatment is to dehydrate partially the colloidal matter which does not immediately become rehydrated on the addition of water during the mixing.

This slow rehydration of clay is of every day occurrence, for it is very noticeable that after a drought the soil does not become sticky immediately following rain. On the other hand the agriculturalist knows that clay lands become so sticky that they are unworkable during continued wet weather.

The roads have been greatly improved in some sections by a proper mixing of sand and clay. Pure sand is too loose, while pure clay becomes too sticky during a rainy period. In the proper proportions the clay is the binder while the sand produces the porosity necessary in order that the water may run through. The sand also dilutes the clay to the point where the latter does not become too sticky.

* Fremy's Encyclopédie chimique, 67 (1888).

Adsorption by Clays. — Owing to the possibility of chemical reactions between the clay and the adsorbed substances, the phenomena here are much more complicated than is ordinarily the case with many colloidal systems. According to Sullivan* changes between the radicals are often involved. For instance when acid or neutral salts are adsorbed, sodium, potassium, and magnesium from the clay may be released or dissolved, while an equivalent amount of the adsorbed basic radical remains with the clay. The addition of alkaline solution is still more complicated. Not only may there be free alkali but basic solutions may be formed because of the hydrolysis of salts of a strong base and a weak acid, *e.g.*, carbonates and phosphates. Three different reactions are now possible. First, the free alkali may react with the colloidal silica. Second, the silicate radical from the clay may form insoluble salts with the adsorbed base. Third, the sodium, potassium, or magnesium displaced from the clay may form soluble carbonates and phosphates, and these salts in turn be adsorbed by the clay constituents.† These reactions are of great importance in the study of the fertilization of the soil. It has been claimed that the addition of lime not only neutralizes the undesirable acids, but also renders the potassium of the clay available for the plant.

The property of adsorption is utilized in the determination of the amount of colloidal matter in clays. Malachite green is often employed for this purpose.‡ The basic radical of the dye forms an insoluble salt with the acid radical of the colloidal clay. The amount of dye taken up is compared with that adsorbed by a standard clay of known colloidal content.

Deflocculation. — This is a term employed to indicate an increase in the colloidal properties, and usually involves a lowering in the value of n. The principal defloculants for clays are alkalis, or salts that by hydrolysis give alkaline reactions. Chiefly among the latter are sodium, potassium, and ammonium carbonates, oxalates and phosphates. According to Ashley sodium carbonate may react as follows:

$$Na_2CO_3 + \text{Cagel} \rightarrow CaCO_3 + \text{Nagel}.$$

The sodium gel is soluble and probably acts as a protective colloid, hence it is possible to have a suspension of clay formed that is relatively stable. However too great concentrations of the deflocculating agent may cause recoagulation and precipitation of the mixture. Tannin acts as a deflocculant for clays containing iron. It appears to take

* U. S. Geol. Survey, Bulletin 312 (1907).

† Van Bemmelen, Landw. Vers. Stat., **23**, 267 (1879).

‡ Ashley, U. S. Bureau of Standards Technological Papers, **23**, 40.

the iron into solution forming a soluble, and probably a protective colloid. Certain dyes also make good deflocculants.*

Soils. — Beside the constituents of the clay soil contains organic colloids, the most important of which is humus. This substance is partly composed of acids, and is formed as a result of the decomposition of organic matter. Humus is a good culture substance for bacteria and micro-organisms beneficial to the soil. Humus may also act as a protective colloid for other substances, but its chief function, beside being a depository of nitrogenous matter, is to adsorb moisture and plant food, such as nitrates, potassium and ammonium carbonates, and phosphates. The amount of moisture retained by the soil in dry weather is directly proportional to the percentage of colloidal substances; therefore lean clays are especially benefited by the presence of humus, because they are deficient in inorganic colloidal matter.

Humus, being negatively charged, is coagulated into a gel by basic substances such as lime. The objection raised by some agriculturalists to adding lime and barnyard fertilizer to the land at the same time seems to be well grounded. The lime should be added first and allowed to become thoroughly air slaked (changed to carbonate) before the organic matter is put on, otherwise the humus may be rendered too insoluble to function in a manner beneficial to the soil.

* Ashley, *l. c.*

CHAPTER XX

COLLOIDS IN SANITATION

Perhaps in no field is colloidal chemistry of so much importance as in that of biology. A résumé of the work done would require space far beyond that which is available here. Therefore a very limited field, included under the rather general head of "Sanitation," has been chosen for illustration because of its great importance to both chemists and biologists. This field involves those smallest of living individuals known as bacteria. A bacterium consists fundamentally of some protoplasm enclosed in a nitrogenous membrane. Bacterial cells suspended in water or in water solutions are colloids. They migrate* toward the anode under the influence of an electric current and are therefore negatively charged. They are precipitated by ions of the heavy metals, by aluminium and ferric ions, and by hydrogen ions, but are not so sensitive as the so-called suspensoids.† One of the objects of the sanitary purification of water is the removal of these bacteria, particularly of those which may cause diseases.

Natural waters may contain other colloids besides bacteria. For instance water collected from a swampy region is usually colored. This coloring matter consists largely of organic colloidal material, together with some substances in true solution. The colloids are positively charged except when the water is highly alkaline, a condition which probably causes the charge to become negative. Waters may also carry more or less clay or silt which, if in small enough particles, cause "turbidity." These particles are negatively charged. The precipitation of colloidal material in water, either coloring matter or that causing turbidity, sometimes takes place under natural conditions. For example, when a highly turbid stream meets another stream carrying acid mine waste the hydrogen ions in the latter cause a precipitation of the negatively charged clay or silt with the formation of a deposit which may become sufficiently large to affect the direction of the stream flow. Muddy river waters on reaching the ocean may deposit suspended matter to form a delta. This is an instance of the precipitation of colloids by salts. A colored water from a swamp may enter a stream containing colloidal clay. The positive and negative charges are

* Bechhold, "Die Kolloide in Biologie und Medizin," p. 189.

† Taylor, "The Chemistry of Colloids," p. 304.

neutralized and partial precipitation results, leaving in the water an excess of one or the other colloid. For this reason it is very rare to find a water which is both colored and turbid, a fact that is easily explained on the basis of colloidal chemistry.

The artificial purification of water furnishes an illustration of the application of colloidal chemistry to industry. There are two general methods in use on a large scale. The older, known as slow sand filtration, consists fundamentally in passing the water through a bed of sand on which has formed a jelly-like mass (called a schmutzdecke) made up of living organisms and dead organic matter which have been removed from the water. Organisms increase very greatly in number in schmutzdecke. This method removes practically all the bacteria and the turbidity, but only a portion of the color. This removal depends on the precipitation of the colloids, first, by contact with the particles of sand, and second by the colloidal schmutzdecke. The latter is by far the most important factor since the filtration is not efficient until the schmutzdecke is well formed. On account of the fact that only a part of the positively charged coloring matter is removed while practically all of the bacteria and other negatively charged colloids are retained by the filter, it is probable that the jelly-like mass contains mainly positively charged colloids. Some of the dissolved color is undoubtedly adsorbed by the schmutzdecke or by the sand.

The more modern method of water purification and one that is applicable not only to municipal supplies but also may be used in an institution or a factory, is that known as "mechanical" or "rapid" filtration, or sometimes as the "American system." Both gravity and pressure filters are used but the principle involved is the same in either case. In this method some coagulant, generally aluminium sulphate, sometimes iron sulphate, is added to the water. The alkali already present in the water or that artificially added, usually as soda ash, causes a precipitation of the positively charged colloidal aluminium (or iron) hydroxide. The water is then passed through a basin in which the hydroxide is coagulated and finally at a rapid rate through a bed of sand. By this process, practically all of the turbidity and color are removed together with a very large percentage of the bacteria.

The method depends on a number of colloidal reactions. First, there is formation of a positively charged colloidal hydroxide. Second, this hydroxide reacts with the negatively charged bacteria and clay or other colloids. Third, the excess colloidal aluminium hydroxide is precipitated by agitation. Fourth, the positively charged coloring matter is precipitated by the negatively charged sulphate ion. Fifth, any color in true solution is adsorbed by the hydroxide.

Catlett * has recently reported an instance in which these principles were applied to solve a problem in water filtration. The water was unusual in that it was both highly colored and highly turbid. It was a mixture of two waters which reached the filter plant before sufficient time had elapsed for mutual precipitation of the colloids. Alkali had to be added to precipitate the required amount of alum. In general practice the water is dosed with the alkali previous to the addition of the alum. In this case poor results were obtained, the color not being completely removed. The trouble was remedied by adding an excess of the alum first. This gave an opportunity for the aluminium and sulfate ions, both of which have high precipitating power, to act. Alkali was then added to precipitate the hydroxide, and the process continued as before. This change yielded a very satisfactory water.

It is known that a water containing a considerable amount of sewage pollution requires more alum for purification than an unpolluted water having the same turbidity and color. It has been suggested that this is due to the presence of protective colloids in the sewage.

The methods of sewage purification furnish another example of applied colloidal chemistry. The main object of such purification at the present time is to produce an effluent which can be disposed of without causing any nuisance, in other words a relatively stable effluent. Approximately complete nitrification is also sometimes aimed at, but sufficient stability can usually be attained without this. The putrescent matter in sewage consists chiefly of nitrogenous organic compounds, a large proportion of which are present in colloidal solution, and are negatively charged. Methods of sewage purification must therefore involve essentially the precipitation of this colloidal material.

The old method of chemical precipitation, now limited to the treatment of factory wastes, depends on the same principles as the rapid filtration of water described above. The modern method of intermittent sand filtration, and the still more recently devised trickling filters, are of paramount importance to the sanitarian. These processes depend on the precipitation of the colloidal material in the sewage by contact with sand in the first case and with crushed stone in the second.† In addition there is also present on the surface of the stone a gelatinous slimy growth of micro-organisms, colloidal in nature, which is really the essential feature of the trickling filter process, and is responsible for the precipitation of the colloidal putrescible material in the sewage. The "colloiders" devised at the Lawrence Experiment Station are somewhat of the same nature.

* Engineering Record, **73**, 741 (1916).

† Stein. Engineering Record, **69**, 525 (1914).

The most recent method for sewage purification, that known as the activated sludge process, is different in principle. It was found by Fowler, and more carefully studied by Ardern and Lockett in England, by Bartow in this country and by others, that if a sample of sewage was aerated for a long period, several weeks, clarification and finally nitrification took place. If some of the sludge from this settled sewage was added to a fresh sample and air applied again, the time of purification was greatly reduced. Repetition of this process finally gave satisfactory results in a few hours. The sludge used to inoculate a fresh batch of sewage is known as "activated sludge." As far as the removal of colloidal material is concerned, and this is all that is desired in many cases, the method has been supposed to depend on mechanical precipitation. In the opinion of the author, based on the fact that the presence of activated sludge is essential even to mere rapid clarification, the process depends not only on the mechanical effect on the colloids but also involves the precipitating action of micro-organisms, or more likely their enzymes.

Another application of colloidal chemistry is in the study of the mechanism of disinfection.* The first step involved consists in the taking up of the disinfectant by the bacteria. This is followed by a poisoning action on the cell. As far as we know at present the former is the only part with which colloidal chemistry is concerned, for the poisoning is probably a very complex action. When bacteria, which can be regarded as colloids, are suspended in water and a disinfectant added, the latter may be distributed according to three methods, which are comparable to the action in the taking up of dyes by fibres. There may be (*a*) a chemical compound formed between the disinfectant and the bacteria, (*b*) a distribution according to Henry's law or (*c*) a distribution according to the adsorption law. This latter is tested by application of the adsorption equation, $x = kc^{\frac{1}{n}}$, where x is the amount of disinfectant adsorbed per unit of adsorbing substance, c is the concentration of the adsorbed material in the water phase, and k and n are constants. Comparatively little data is available on which to discuss the three possibilities. This is due partly to the difficulty in measuring such minute amounts of any disinfectant removed by the organisms, and partly to the fact that many of the best disinfectants are emulsoids, which are much more difficult to study than are those giving true solutions.

Some data has been obtained by Herzog and Betzel † using yeast cells

* Bechhold, "Die Kolloide in Biologie und Medizin," pp. 363–379, also, Bechhold, Zeitschr. f. Chemie und Industrie der Kolloide, **5**, 22 (1909).

† Zeitschr. f. physiol. Chem., **67**, 309 (1910).

with chloroform, silver nitrate, and formaldehyde, and by Reichel* using phenol and bacteria. The conclusions reached were that formaldehyde formed a chemical compound with the cells, that phenol was distributed according to Henry's law, and that the taking up of chloroform and of silver nitrate by yeast cells followed the adsorption law. A study has recently been made in the author's laboratory of the distribution of formic acid between water and bacterial cells. The adsorption equation was found to hold very closely. The disinfection was shown to be due to the adsorbed hydrogen ions,† the action being greatly influenced by the presence of salts in solution, but the further mechanism of the reaction has not been ascertained. It is firmly believed that a more complete study of disinfection from the colloidal standpoint will be productive of results which are not only of theoretical interest but also of great practical importance.

* Biochem. Zeitschr., pp. 149, 177, 201 (1909).

† Norton & Hsu, Journ. of Infect. Diseases, **18**, p. 180 (1916). The distribution results have not been published.

SUBJECT INDEX

INDEX OF AUTHORS